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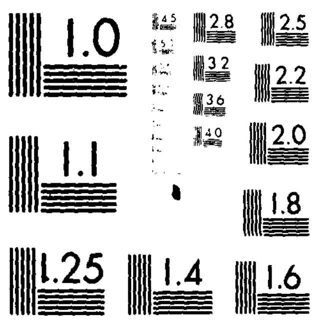

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LRSM

FIFTEENTH ANNUAL
TECHNICAL REPORT

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1 June 1974 to 31 May 1975

LABORATORY FOR RESEARCH ON THE STRUCTURE OF MATTER

UNIVERSITY OF PENNSYLVANIA

PHILADELPHIA, PENNSYLVANIA

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I. INTRODUCTION

The Laboratory for Research on the Structure of Matter (LRSM) is the official name applied by the University of Pennsylvania to its Materials Research Laboratory, an interdisciplinary research and educational program in the materials sciences, and to the building in which most of the work is done. Operating with a total budget of about 4.5 million dollars, the LRSM program has the active participation of about 44 faculty members, 42 post-doctoral fellows, 113 graduate students, and 35 full-time professional, technical, administrative, and clerical personnel. Approximately 200 scientific and technical publications are produced each year. An important part of the program is the operation of 11 Central Facilities, equipped with specialized apparatus and in most cases employing permanent technical staff.

The LRSM at Pennsylvania has become a successful and well-known center for materials research, and is at the forefront of the work in this field. The materials program in the LRSM includes the generation and study of new materials with new and exciting properties; e.g., polymeric sulfur-nitride, $(SN)_x$, the first metallic polymer, amorphous magnetic materials, one-dimensional organic metals, intercalated graphite, etc. In addition and of equal importance, a considerable fraction of the LRSM effort is directed toward improvement of existing materials and materials processing including for example working toward a solution of the important problem of embrittlement of steels, work on chemical and extractive metallurgy, and a major program in surface science. These programs are characterized by a broad based experimental and theoretical approach spanning the disciplines of Physics, Chemistry, Metallurgy, and Electrical and Chemical Engineering. Underlying the entire program is a philosophy of careful and well-characterized materials preparation. The University of Pennsylvania LRSM is broadly known for this emphasis on quality materials and has set a standard for others to follow.

II. THE LRSM THRUST AREAS

The research programs in the LRSM fall generally into five major Thrust Areas:

1. Molecular Crystals
2. Surfaces and Interfaces
3. Materials Failure Criteria
4. Chemical and Extractive Metallurgy
5. Electronic and Magnetic Materials

The implied focusing of the research into coherent thrust areas at the Penn MRL is evolving naturally and at a satisfactory rate. Our view is that a healthy thrust area should have a coherent core consisting of a group of faculty members working toward solution of a common defined problem which is of a scope larger than that traditionally attacked by a single research investigator. A broad approach, typically using a variety of experimental and/or theoretical techniques, is generally involved. Around each of these cores we envision related work which falls into the same thrust area, but which is peripheral to the central core.

Some work outside the core program must continue to receive support, since a breadth of interest and avoidance of narrow specialization is necessary to insure the proper future scientific evolution of the program. At present we have four focused thrust areas (Chemical and Extractive Metallurgy, Molecular Crystals, Surfaces and Interfaces, and Materials Failure Criteria). The fifth area, Electronic and Magnetic Materials, is more diffuse and has traditionally been the origin of new programs (the Surface program and the Molecular Crystals program both originated there); this process is continuing.

1. Molecular Crystals

This program stands on the border between solid state physics and synthesis organic and inorganic chemistry. It combines the enormous power of chemistry to provide new materials, and the sophistication of solid state physics to measure and interpret electronic properties, in an effort to learn to predict properties and design compounds that would be useful in technology. Success in this area requires active collaboration between physicists and chemists, and we believe we have achieved highly effective cooperation.

In addition to its major activity, preparing and studying new materials exhibiting novel solid state properties, a principal objective is to obtain sufficient fundamental understanding to allow the achievement of desired solid state properties by chemical design and synthesis of the molecular units.

An important part of the research in this area involves a class of solids known as organic charge transfer salts, plus other pseudo-one-dimensional systems which are evolving out of the interdisciplinary program. The short range goal is to prepare and study these materials, especially instabilities in the one-dimensional electron gas which lead to the metal-insulator (Mott) transition, and the Peierls-Fröhlich semiconductor-superconductor collective state. The long-range goal is to arrive at an understanding of theory and a command of synthesis such that useful technological materials can be predicted, designed, prepared, and put to use. At present attention centers on the synthesis and study of new organic charge transfer salts (analogous to the TCNQ salts), organometallic salts, and polymers. The principal names associated with this area are Heeger and Garito, of Physics, with close collaboration in the synthesis of new materials with two faculty members from Chemistry: Cava and MacDiarmid.

The LRSM has created a central facility for organic crystal growth which is devoted almost entirely to this Thrust Area, and which is functioning very successfully.

The LRSM has in addition a strong and far reaching program on non-metallic molecular crystals. The work is both experimental and theoretical, and a wide range of molecular materials are being synthesized and studied. Of particular interest to this group also is the study and characterization of pseudo-one-dimensional electronic systems, and Hochstrasser's group in particular is continuing its pioneering work in the area of energy transport in molecular crystal systems.

This research is mainly a wide ranging spectroscopic study of organic molecules in crystalline and quasi-crystalline aggregates (including liquids). By studying excitations in neat and mixed molecular solids and liquids one is trying to bridge the gap between the understanding of microscopic systems, starting from small molecules, and that of macroscopic systems like a crystal, or a liquid. The nature of the dynamic intermolecular interactions goes back to the intricate nature of the constituent molecules. Our present crude chemical and structural information on molecules will rarely predict intermolecular dynamics so we have to study empirically such interactions in the most appropriate systems: Isotopically and chemically mixed crystals and liquids.

Within the Molecular Crystals thrust area a new sub-group is emerging. Hochstrasser, Smith and Topp are organizing for a concerted attack on photophysical properties of unusual organic solids using spectrally sharp tunable lasers. Obviously the progress to date and the current level of activity in molecular photophysics and chemistry signal the emergence of an exciting new aspect of molecular crystals research at LRSM - one that will significantly widen the scope of these materials.

2. Surfaces and Interfaces

The primary goal of the Surfaces and Interfaces Thrust Area is to develop an understanding, on a microscopic level, of the bonding of and the interaction between adsorbed species on a solid surface. The core of the thrust is directed specifically to questions concerning the interaction of simple molecules, such as H_2, CO, and C_2, with metal atoms of the late transition series when these atoms are in a variety of well-characterized surface environments. Such systems are simple enough to be amenable to experimental and theoretical analysis - both of which are imperative if progress is to be made - and at the same time are of considerable current interest in industrial processes.

A variety of experimental and theoretical techniques are being employed by thrust area members. One must study experimentally the structure of the bonding surface, the nature of reacting species, bonding configurations of reactants, the kinetics of the formation of surface species, etc. Theoretical effort must focus on the phenomena themselves as well as on the interpretation of experimental techniques and results.

The core of the surface thrust area involves principal investigators in three departments - Physics, Chemistry, and Metallurgy and Materials Science. This breadth of expertise allows us to investigate the interaction of adsorbates with a single transition metal atom isolated in a metallo-organic complex, with a sharply etched tip having many facets, and with a nearly perfect macroscopic single crystal surface. This range should lead to considerable insight into the effect of metal coordination on chemisorption and catalysis.

The identification of molecular species on a surface, the nature of the chemical binding, and the underlying quantum mechanical structure of the substrate is being investigated using photoemission spectroscopy (Plummer and Gustafsson) the surface sensitivity of the technique, the fact that it can be used to study the high lying quantum states entering into bonding phenomena, and its non-destructive action on the surface itself combine to make it an exceptionally powerful tool.

The properties of clean substrates are also being investigated with field emission spectroscopy (W. Graham). Work in progress is focused on Ni, Mo, and Si. It is known that field emission measures particular aspects of the surface density of states. The geometry of the adsorbate and the location of the active site will be investigated by field ion microscopy, field desorption microscopy, γ-γ angular correlation (Caspari), infrared spectroscopy (Burstein) and angular-energy resolved photoemission spectroscopy (Plummer and Gustafsson). The latter technique shows great promise of being able to determine not only the symmetry of the bonding site but the spatial distribution of each orbital involved in the surface complex.

Chemisorption and the associated modified chemical reactivity are being studied primarily by groups in chemistry (Fitts, Brennen and Myers). These groups share with the surface structure and theoretical groups a common focus in exploring how chemisorption processes alter small molecule reactivity by directing the nature of reaction products, and altering the kinetics and mechanism for these fundamental reactions.

The interaction of small molecules (CO, NO, O_2, N_2, H_2, N_2O, SO_2) with metallo sites ($Mn^{II, III}$, $Fe^{II, III}$, Ni^{II}, Cu^{II}) in well-defined rigid ligand environments are being systematically examined (Wayland). Varying the metallo site used in binding small molecules is observed to produce diverse electron distributions such as NO^+, NO^-, O_2^-, O_2^{2}. The interrelationships of chemisorption-induced electronic changes and modified chemical reactivity are developing. A general model of metal binding and chemisorption of diatomic molecules is evolving from combined experimental and theoretical studies.

Considerable effort in the thrust area is focused on gaining a theoretical understanding of the basic phenomena as well as aiding in the interpretation of experimental results (Schrieffer and Soven). Much of this work deals with the following types of problems: 1) the prediction and interpretation of angular-resolved photoemission spectra of atoms and small molecules chemisorbed on transition metal substrates, 2) the development of self-consistent scattered wave calculations of the electronic structure of transition and noble metals in film geometry, 3) the investigation of the Born-Oppenheimer potential energy function for chemisorption and surface chemical reactions of small molecules on transition metal surfaces, and 4) the identification of those features of the substrate that govern its chemical reactivity. The rationale for these projects, in concert with the experimental program, is 1) to understand the geometry of the adsorption site(s) and directionality of the chemisorption bonds; 2) to provide a first principles understanding of the clean surface so that the parameters of approximate (LCAO) model Hamiltonians can be fixed for use in the more complex problems of chemisorption and surface reactions; 3) to further the development of a quantum mechanical model for understanding chemisorption bonding, surface diffusion and surface chemical reaction involving small molecules on metal surface.

3. Materials Failure Criteria

This area is deeply rooted in a major field of technology, and reaches into the disciplines of physical metallurgy, solid state physics, and chemistry for its scientific understanding. The core problem being attacked is the effect of impurities on the fracture behavior of structural alloys, and specifically the phenomenon of temper embrittlement. This is a long-standing problem encountered in some alloy steels, notably those used in large cross-sections such as turbine shafts and thick-walled pressure vessels. Certain

heat treatments, or service at elevated temperatures, can lead to abnormal brittleness and sometimes to catastrophic failures. It is well-established that the effect originates in the collection of certain impurity elements at the grain boundaries; however, the mechanism of the segregation, the reason for the connection between impurity segregation and brittleness, and effective means of controlling the brittleness remain unknown.

The program on embrittlement was formed from the necessity to attack the problem of residual elements in steels from a number of points of view, employing disciplines outside of traditional physical metallurgy. The program has a unified design, worked out in a collaborative way based on research that was being carried out for a number of years by McMahon and Pope. In essence, the problem was developed to the point where further progress was being inhibited by lack of knowledge in several important areas. Hence the four new members were acquainted with the problem and with the needs for their contributions, and the program developed into a true thrust area.

The problem can be stated as follows: Elements from Groups IV to VI, when present in alloy steels in trace amounts, tend to become concentrated in grain boundaries, particularly when a steel is heated for prolonged periods in the temperature region of ferrite + carbide stability. The results of this are reduced fracture toughness and increased tendency for cracking when the steel is stressed in aggressive media or at high temperatures.

Recent work at the LRSM by McMahon (MMS) has led to a new idea about the origin of the segregation, and has inspired a major experimental and theoretical program on temper embrittlement and related impurity effects in structural materials. The approaches being taken include: studies of the effect of impurity additions on the initiation and propagation of intergranular cracks in high-purity CrMo and CrMoV steels (Pope; MMS); the effect of variations in alloy content on embrittlement of steels containing fixed amounts of C and P, Sn, or Sb (McMahon; MMS); a determination of the effect of alloying elements on the chemical activity of dissolved embrittling elements (Belton; MMS); experimental study of the segregation to free surfaces in high vacuum of embrittling elements in high-purity alloys (W. Graham; MMS); and a theoretical and experimental approach to the mechanism by which the embrittling elements lower the cohesion in alloys (Egami; MMS). It will be seen that the approaches include conventional physical metallurgy techniques, thermodynamic methods, surface science, and theory; the faculty members working on the project have backgrounds in metallurgy, physics, physical chemistry, and applied physics.

The long range and short range goals are identical: to develop sufficient understanding of impurity effects at grain boundaries to design alloy compositions and heat treatments that will significantly improve the performance of structural materials.

Other efforts falling under the general heading of materials failure criteria include studies of the origin of the mechanical strength of ordered alloys, of the nature and prevention of mechanical damage due to cyclic loading, of phase transformations and mechanical properties of amorphous metals, and the deformation of polymers, emphasizing low-temperature surface effects. (Pope, Laird, Brown; MMS).

4. Chemical and Extractive Metallurgy

It has recently been stated that the wealth implicit in American mineral resources is no longer a bonanza which lies in the ground for the taking - it now lies in the extractive technology employed. Present-day metallurgical extractive and refining technology is rapidly becoming inadequate due to the declining quality of available ores, the demand for recycling of scrap metals, the need for lower impurity levels in refined metals, and the increasingly stringent air and water pollution controls. With rare exceptions, the development of new processes depends upon the discovery of new chemical and process principles.

Deterioration and eventual destruction of materials by reactions with their environment contribute extensively to the depletion of our material resources. From a financial viewpoint, it has been estimated that the total cost of corrosion and corrosion protection in the United States is 8 billion dollars annually. Corrosion-resistant materials are especially needed for high-temperature applications such as gas turbines.

Chemical and Extractive Metallurgy is an applied science concerned with the efficient production and conservation of metals. The major objective of the Chemical and Extractive Metallurgy Thrust Area is to increase basic knowledge in those areas of high-temperature chemistry which are important for technological advances in extractive metallurgical processes and in corrosion-resistant materials. The selection of research projects is strongly influenced by their pertinence to specific technological problems. Current projects are concentrated in five research areas, in which basic studies are needed for future technological advances. These areas are multicomponent metallurgical solutions, interfacial kinetics, new electrochemical sensors, high-temperature corrosion and high-temperature vapor species.

This is a small group, but it is now the largest similar program at any U. S. University. Although a range of topics is under investigation, and the faculty have quite different backgrounds and research specialties, the effort is highly cooperative. The faculty members and students work closely together, and a regular weekly internal seminar is held to present and discuss the progress of current research.

5. Electronic and Magnetic Materials

This area is more diffuse than the other Thrust Areas; the cooperative effort is generally confined to groups of two or three faculty members and their students. It includes work of very high quality and makes contributions of great value to the general health of the program. Both the Molecular Crystals and the Surfaces and Interfaces Thrust Areas include members whose basic interests can be properly described as electronic properties, and who in previous years would have been included in this Area.

In magnetic materials, interest centers on amorphous magnetic alloys. These materials, made in the form of narrow ribbons by very rapid cooling from the liquid state, have been found to have soft magnetic properties that make them competitive with the best available commercial materials. The research includes the production of new alloys (Maddin; MMS), the measurement of magnetic properties and exploration of ways to improve properties, and an attempt to understand the properties. (Egami, C. Graham; MMS). This program is unusual at the University in that the short-range goal is to make a useful material, and the long-range goal is to understand why it works. Other work in magnetism includes the determination of the atomic structure of amorphous oxides from magnetic measurements, and several projects on permanent magnet materials, especially MnBi and $SmCo_5$; these all depend on the facilities of the LRSM high field laboratory.

Burstein's (Phys) wide-ranging program in Raman scattering in solids includes work in semiconducting materials as well as in dielectrics and semimetals. Also included in this area is a program in superconducting phenomena, particularly Josephson effects and time-dependent non-equilibrium effects, some of which are applicable to the detection of high-frequency radiation (Langenberg; Phys). Finally, there is a comprehensive theoretical program on magnetic and other phenomena in random and amorphous alloys. (Harris, Phys).

There is a series of overlapping projects on various aspects of semiconducting materials and behavior, especially in the IV-VI compounds. Among the topics are noise power; PbS-Si heterojunctions, with emphasis on device applications; band structure calculations in IV-VI compounds and their alloys, with special reference to the elastic properties; localized states in IV-VI compounds; modulation spectroscopy measurements on various old and new semiconductors; and amorphous semiconductors. The faculty involved are Fischer, Rabii, (EES): Langenberg, (Phys); and Nixon, (Chem).

Included in the Electronic and Magnetic Materials area is the program on Intercalated Graphite compounds. This work is new to the LRSM and is developing into a large interdisciplinary research effort on this interesting and potentially useful class of materials.

III. RESEARCH HIGHLIGHTS, 1974-75

Some significant results of the LRSM research program in 1974-75 are presented here. They are arranged by thrust areas, and the principal contributing faculty are indicated.

1. Molecular Crystals

A. Polymeric Sulfur Nitride, $(SN)_x$: The First Metallic Polymer

The achievement of fully oriented epitaxial thin films of the electrically conducting metallic covalent polymer $(SN)_x$, polymeric sulfur nitride, was a focal point of the work on this inorganic polymer. This represents the first reported case of fully oriented epitaxial growth of thin films of any polymer. That this was possible for the metallic polymer $(SN)_x$ is of particular significance because of the anisotropic optical and electronic properties of this system. (Garito, Heeger, MacDiarmid).

$(SN)_x$ was prepared in analytically pure form at Penn. The synthetic method involves first the isolation of pure colorless crystals of S_2N_2 which subsequently undergo solid state polymerization in vacuum at room temperature to give lustrous golden crystals of analytically pure $(SN)_x$. X-ray studies have recently revealed the $(SN)_x$ structure to consist of almost planar chains of alternating sulfur and nitrogen atoms. Comparison of the $(SN)_x$ structure and that of the precursor S_2N_2 has led to a detailed understanding of the solid state polymerization process.

Recent studies show that pure $(SN)_x$ has a room temperature electrical conductivity of about 3×10^3 ohm^{-1} cm^{-1}, which is of the same order of magnitude as an ordinary metal such as mercury increasing in values greater than 5×10^5 $(\Omega\text{-cm})^{-1}$ at low temperatures.

Highly reflective golden thin films of $(SN)_x$ can be grown on glass or polymer substrates by direct sublimation of $(SN)_x$ crystals. The resulting films have the same crystal structure as the parent crystals and have similar electronic and optical properties. Optically reflective films have been grown on a variety of substrates. On glass substrates, polycrystalline films grow preferentially oriented with the mean plane $(\bar{1}02)$ of the $(SN)_x$ polymer chains parallel to the substrate surface. Complete epitaxial growth with $(SN)_x$ polymer chains oriented in a single direction within the plane is found for example, on teflon, mylar, and polyethylene substrates.

The anisotropic optical and electronic properties of the $(SN)_x$ oriented films are of potential technological use. The techniques developed in the LRSM allow $(SN)_x$-plastic substrate composites to be fabricated in order to explore particular mechanical, electrical, or optical features of the

composites. For example, the large optical anisotropy of the oriented epitaxial films suggests the possibility of useful applications in integrated optical systems.

Theoretical studies of the electronic band structure of $(SN)_x$ were carried out under the direction of Prof. Paul Soven. The results indicate band widths of order one to two eV and indicate a somewhat complicated three dimensional band structure.

Current solid state studies at Pennsylvania are addressing the central question of the actual dimensionality of the electronic properties of $(SN)_x$. Although the chain-like structure suggests a one-dimensional electronic system, detailed studies show that substantial coupling takes place between $(SN)_x$ chains. The results indicate $(SN)_x$ should not be considered as strictly one dimensional but rather should be approached from the point of view of an anisotropic solid with a two, or possibly, three dimensional electronic band structure.

B. TTF-TCNQ

Professors Heeger and Garito and their colleagues have put considerable effort into development of a complete experimental picture of the physical properties of the organic metal (TTF)(TCNQ). As a highly conducting organic salt which remains metallic even at relatively low temperatures, this system is at the focus of work directed toward understanding the nature of the metallic state in organic conductors. The pseudo one-dimensionality of the electronic properties has been established experimentally through measurement of the optical and electrical anisotropy, and is an exciting and novel feature from a theoretical point of view because of the well-known predictions of dynamical instabilities of one-dimensional metals.

The studies of the electrical transport in TTF-TCNQ have been extended from dc through optical frequencies to provide a broader picture of the phenomena involved. The existence of a gap in the dielectric excitation spectrum of TTF-TCNQ is of central importance to understanding the origin of the remarkable transport properties of this organic metal. The energy gap in the infrared, together with the relatively large dc and microwave conductivities, imply a correlated many-body state in which the low frequency conductivity results from a collective mode. Analysis leads to a collective mode lifetime which is enhanced over the single-particle scattering time by at least two orders of magnitude at room temperature and more than three orders of magnitude near 60 K. This comparison represents one of the clearest indications of coherence in the "metallic" state of TTF-TCNQ. If the collective mode were of zero width, the dc conductivity would be infinite and the system would be a true superconductor. However, because of the absence of long range order in one-dimensional systems (together with the possibility of intrinsic dissipative processes in the Fröhlich mechanism),

the superconducting fluctuations lead to a delta function-like collective mode near zero frequency having finite width.

Very recently the existence of the Peierls distortion has been confirmed with x-ray studies carried out in a collaborative study between the Penn group and Dr. R. Comes and co-workers at Orsay. The superlattice has been observed at low temperatures with the dimensions of the superlattice unit cell being 2a x 3.7b x 2c. The fact that the superlattice period along b is evidently incommensurate with the underlying lattice is particularly important in that it implies that the distortion is driven by the soft $2k_F$ phonons and, above 58 K, is the source of the high dc conductivity, the energy gap, and the overall features seen in $\sigma_1(\omega)$ and $\epsilon_1(\omega)$. As the temperature increases the superlattice Bragg peaks broaden into one-dimensional diffuse scattering streaks indicative of the Peierls-Fröhlich state in the fluctuation regime.

In summary the Peierls distortion has been demonstrated in TTF-TCNQ. The associated electronic optical, infrared, and magnetic data indicate that above 58 K, TTF-TCNQ has the properties of a one-dimensional superconductor in the fluctuation regime with a mean field scale temperature of order 400 K.

C. Spectroscopic Studies of Molecular Crystals

As a result of on-going research at LRSM on photophysical processes in molecular crystals (Hochstrasser) there has arisen the concept of using near and mixed crystals as materials for molecular design and isotope enrichment. Smith and Hochstrasser have already made significant progress in this exciting new area of materials science: Recently, the first low temperature (1.6 - 10 K) isotopically selective photochemical reaction in a molecular crystal was performed here. The selective optical excitation and generation of molecules rich in naturally abundant isotopes, in this example ^{13}C, ^{15}N and ^{2}H, was demonstrated using a tunable dye laser. The system used was s-tetrazine which absorbs red photons to yield HCN and N_2 even at very low temperatures.

2. Surfaces and Interfaces

Plummer and Gustafsson using ultraviolet photoemission have shown that the proper identification of the energy levels of adsorbed molecular CO (and presumably many other systems) can be made by measuring the photoionization cross section of each energy level as a function of photon energy, for adsorbed CO and gas phase CO. These measurements have shown that the photoionization cross section as a function of photon energy is a reliable finger print of a specific molecular orbital.

A significant part of the theoretical effort is directed toward the development of practical and accurate ways of predicting such molecular

properties as binding energy curves and photoemission cross sections. A major advance has been made by Bryan Danese, initially in collaboration with J. Connolly at the University of Florida and for the last year with the theoretical group at Penn. Danese and Connolly incorporated the so-called non muffin-tin corrections into their binding energy curves, and Danese and Schrieffer have done the same thing for the one electron levels. Calculations have been completed for several first row diatomics (C_2, N_2, Ne_2, and CO) with very encouraging results. In particular, very satisfactory binding curves have been obtained for these molecules, and the one electron photoionization spectra of CO agrees with experiment to roughly 0.3 eV for valence levels and to a comparable percentage for core levels. This level of agreement is far better than that achieved by other techniques.

3. Materials Failure Criteria: Embrittlement of Alloy Steels

A major program on embrittlement of alloy steels has developed within the LRSM. Based on the important initial accomplishments of Profs. McMahon and Pope on the role of critical impurities in the embrittlement process a broad study is underway.

Our understanding of the embrittlement of alloy steels by Group IV to VI impurities seems to have been increasing exponentially in the last several years. During the past year we broke through some important barriers. First, we have determined that, in the cases of Sb, Sn, and P in Ni-Cr steel, the temper embrittlement is an equilibrium phenomenon, rather than being a non-equilibrium (i.e., ultimately transient) process. Second, we have identified the primary variables and have shown how they should be dealt with. Finally, we have worked out some of the mechanisms by which particular alloying elements control the segregating tendency of Sb, Sn, and P. From our current viewpoint we can see no more serious barriers in the way of a full understanding of the phenomenon, and it appears that the full solution to this classical metallurgical puzzle will be worked out in the next few years.

The primary variables which determine the degree of degradation of fracture toughness (or shift in transition temperature) are: (1) the amount of a specific impurity in the grain boundaries, (2) the hardness of the steel, and (3) the grain size. Thus, the toughness can be predicted by measurement of these variables and can be controlled by manipulating them.

4. Chemical and Extractive Metallurgy

Significant progress has occurred in our high-temperature investigations of silicate melts, interfacial kinetics and materials corrosion. The majority of pyrometallurgical extraction operations employ slag-metal refining processes, the efficiencies of which are determined largely by the performance of the slag (silicate melt) phase. Current investigations of the structural

and thermodynamic properties of silicate melts are aimed at determining the fundamental structure - property relationships in these melts. The origin of the deviation from ideal silicate mixing in ternary silicate melts has been identified (Gaskell). Experimental results have shown that negative deviations in such melts are caused by preferential association of cations with free oxygen ions and silicate anions. However, as the silica concentration in the ternary silicate increases, the free oxygen ion concentration decreases to zero. When this occurs, positive deviations arise due to cation-cation coulombic interaction through the silicate anions. The magnitudes of such positive deviations are determined by the size of the silicate anions. Because of these two different types of deviations, there exists a narrow composition range in which the two opposing effects cancel. Thus one observes apparent ideal silicate mixing in $CaO-FeO-SiO_2$ and $MgO-FeO-SiO_2$ melts near the metasilicate composition.

Most, if not all, of the important metallurgical reactions occur at interfaces, and a number of our research investigations are directed toward determining the factors which control the transfer rates of species between phases. Of particular interest is the effect of surface poisoning by surface-active dilute solutes on interfacial-reaction rates. For example, the decarburization of liquid iron by CO_2 at temperatures between 1150 and 1600°C is being investigated (Belton). During the past year, experimental studies of this reaction under conditions of carbon saturation, have established that the forward rate is proportional only to the pressure of CO_2. The measured rates are much higher than those previously reported for this reaction, which indicates that previous studies were controlled by transport in the CO/CO_2 gas mixture.

A new class of exciting high-temperature materials are the exceptionally stable transition metal-platinum compounds. To provide the fundamental information necessary to assess their usefulness as corrosive-resistant coatings for the transition metals, studies of the thermodynamic and kinetic properties of these compounds have been undertaken (Worrell). Thermodynamic data for the Pt-Ti, Pt-Zr and Pt-Hf binary systems at temperatures between 800 and 1200°C have been obtained. Results confirm that intermetallic compounds ($TiPt_3$, $ZrPt_3$, $HfPt_3$) in these systems are exceptionally stable. Our measured values for the chemical stabilities of these compounds agree with the predictions of the Engel-Brewer correlation between electronic configuration, phase stability, and crystal structure of alloys. With such thermodynamic data, one can quantitatively assess the chemical stability of these compounds at elevated temperatures and in various environments.

5. Electronic and Magnetic Materials

A. Amorphous Magnetic Alloys

LRSM has taken a leading role in the investigation of the magnetic properties of amorphous alloys prepared in ribbon form by rapid freezing

from the melt. The principal contributors in the work on the magnetic properties of these materials have been Takeshi Egami, P. J. Flanders, and C. D. Graham, Jr.

The fact that amorphous alloys can be ferromagnetic has been known for at least 10 years, and Pond and Maddin (LRSM) reported a method to make amorphous ribbons by quenching a jet of liquid alloys on a rapidly-rotating drum in 1969. The current major excitement began, however, in late 1973 when the Allied Chemical Corp. Materials Research Center announced that they could produce substantial quantities of amorphous ribbons of various compositions, and were actively seeking commercial applications. Their production process is described as a modification of the Pond-Maddin technique. Measurements of the magnetic properties of these ribbons began at LRSM about March 1974. It was quickly established that the ribbons have good d. c. soft magnetic properties: the coercive field is low, generally 0. 1 to 0. 01 Oe; the hysteresis loop is square, with high remanence; the magnetizations are quite high, ranging from 5000 to 17000 Gauss in the compositions made by Allied Chemical. Coupled with the fact that the mechanical properties are excellent, with very high strength and reasonable ductility, and that the production process is simple and should be cheap, it appeared that a major new material was available for multiple uses, such as transformers, transducers, recording heads, etc.

B. Graphite Intercalation Compounds

A major interdisciplinary research effort on the materials science and engineering of graphite intercalation compounds has been initiated. This is a family of well-ordered metallic derivatives of graphite, which show great promise as light weight, room-temperature, low-loss electrical conductors. The principal results obtained in the initial year are summarized as follows:

1. Graphite fibers intercalated with nitric acid exhibit the same fractional conductivity increase as intercalated crystals (roughly a factor of 10). The elastic modulus increases slightly. These results offer promise of realizing a strong, highly conducting composite wire based on intercalated fibers.

2. Synthetic crystals intercalated with BF_3 + F_2 exhibit conductivity increases of 25x, the highest reported to date. This supports the simple idea that fractional charge transfer is correlated with the strength of acid, and suggests that intercalation compounds with room temperature conductivity greater than that of copper are feasible.

3. The metallic nature of acid intercalates has been confirmed by near IR reflectance spectra which exhibit free-carrier plasma edges. The plasma frequency is higher for a superacid compound than for a HNO_3 compound, again suggesting stronger metallic character with superacid intercalation.

4. Graphite powders have been intercalated with SbF_5; powders are attractive because they are cheaper than fibers and because they are more nearly crystalline and thus offer hope of higher ultimate conductivity.

5. Room-temperature thermoreflectance spectra reveal several features suggestive of interband transitions, as well as a strong derivative response associated with the plasma edge. Strong critical point optical response is expected from singularities in a two-dimensional interband energy surface; these singularities are being analyzed to construct a zero-order band model for the intercalation compounds.

IV. THE RESEARCH PROGRAM

In this section we present brief accounts of individual LRSM research projects, including projects supported through LRSM by NSF and projects supported by other agencies.

A. MOLECULAR CRYSTALS

1. Synthesis of Heteroatom Organic Free Radicals

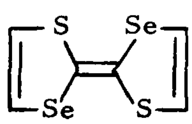
M. P. Cava, Professor of Chemistry

Postdoctoral Fellow: M. V. Lakshmikantham

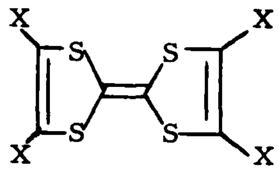
Support: NSF-MRL
NSF

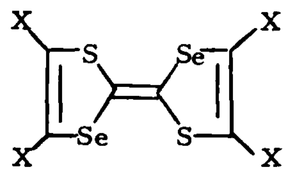
Objective and Approach: Our objective is to synthesize and prepare small organic molecular units for use in highly conducting organic solids. Recent work at Penn on the metallic state properties of organic solids such as (NMP)(TCNQ) and (TTF)(TCNQ) and related derivatives has provided a set of guidelines for productive synthetic studies, especially with stable organic free radicals. On the basis of our previous experience with small heteroatom organic molecules, we plan to continue a series of systematic studies to synthesize a number of TTF related stable radicals for use with TCNQ and related π-acceptors.

Progress: Our major accomplishment has been the synthesis of diselenadithiafulvalene (DSeDTF); the TTF related π-donor. (structure below)



I. We have discovered a new synthetic method for TTF related π-donors which is specific, non-hazardous, and direct. This new process has general applicability and allows for the first time the synthesis of parent S and Se containing TTF π-donors by a synthetic route capable of producing high quality material in quantities sufficient for broad-based experimental studies. Using our new method, we have successfully prepared to date not only DSeDTF but also TTF itself. Additionally, in the course of the syntheses, we isolated the following substituted derivatives as well:

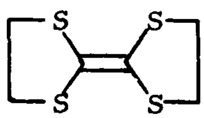


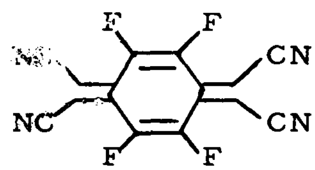


where X = $COOCH_3$ or COOH.

These materials are currently being physically characterized, e. g., solution nmr, ir, etc., and x-ray structure studies are underway with Dr. Voet. Highly conducting charge transfer salts with TCNQ and related π-acceptors are being prepared with Garito and Heeger for solid-state studies.

II. As part of a study with Garito and Heeger to systematically alter the π-polarizability of TTF, we have prepared the first charge transfer salt of tetrahydro TTF using $TCNQF_4$.





This represents an important first example and a series of additional charge transfer salts are currently being prepared.

Publication:

Lakshmikantham, M. V., Cava, M. P. and Garito, A. F., "Organic Metals: Synthesis of sym-Diselenadithiofulvalene", Chem. Commun. 264 (1975)

2. Determination of Crystal Structures by the X-ray Diffraction Method

J. Donohue, Rhodes-Thompson Professor of Chemistry

Research Assistant: B. Sindel

Support: NSF-MRL
NIH
NSF

Objective and Approach: The purpose of this project is to determine the crystal structures of various substances, with the results to include precise information concerning bond distances, bond angles, torsion angles, conformations, thermal vibrations and non-bonded interactions. The substances chosen for study fall into three broad categories: 1) biologically active compounds, 2) compounds of unknown chemical structure, and 3) compounds suited for the observation of intermolecular forces.

In 1) it is important to know the structures of such materials in order to understand how they act in living systems. In 2) quite often studies of chemical reactions give products whose chemical structures are unknown. When these structures are determined by diffraction methods only then can a complete discussion of the reactions themselves be made. In 3) the results should add to our understanding of various interactions between molecules in solids.

Progress: Work was begun on the structure of SN polymer with crystals furnished by Professor MacDiarmid of these laboratories. This work was interrupted for two reasons: first, the crystals were of rather poor quality, being invariably twinned, with the diffraction patterns indicating varying degrees of disorder, and second, the principal investigator was on leave of absence during the spring semester.

The Intercalated Compounds Group of this University drew our attention to a recently published structure for graphite with orthorhombic symmetry and unequal bond lengths. Calculations here have shown that this structure is incorrect, but the way the data were presented in the original paper makes it impossible to draw any further conclusions, except that no evidence for other than the hexagonal structure for graphite is forthcoming.

Following our determination of the crystal structure of dicinnamyldisulfide a literature search of other compounds containing the disulfide linkage has been initiated. The geometry of this feature, which is an important part of most protein structures, will be thoroughly studied. Part of this work included a refinement of the published structure of diglycylcystine. This work is being prepared for publication.

Publications:

Boggs, R. and Donohue, J., "Spermine Copper(II) Perchlorate", Acta Cryst. B31, 320 (1975)

de Titta, G., Edmunds, G., Stallings, W. and Donohue, J., "The Crystal Structure of Biotin (Vitamin H)", J. Am. Chem. Soc. (in press)

Donohue, J. and Chesick, J., "The Crystal and Molecular Structure of Dicinnamyldisulfide", Acta Cryst. B31, 986 (1975)

Donohue, J., "Structure of Graphite", Nature 255, 172 (1975)

Robbins, A., Jeffrey, G. A., Chesick, J. P., Donohue, J., Cotton, F. A., Frenz, B. A. and Murillo, C. A., "A Refinement of the Crystal Structure of Tetraphenylmethane: Three Independent X-ray Measurements", Acta Cryst. (in press)

Stallings, W. and Donohue, J., "The Molecular and Crystal Structure of Permethylbicyclo(3. 3. 1) Nonasilane", Inorg. Chem. (in press)

3. Theory of Electric and Magnetic Properties of Molecules

H. F. Hameka, Professor of Chemistry

Research Assistant: L. V. Haley

Support: NSF-MRL
NSF

Objective and Approach: We are calculating first- and second-order energy perturbations of molecules due to exterior fields, with particular emphasis on electric dipole moments and polarizabilities. Our immediate goal is to calculate the polarizabilities of small molecules (diatomics) with reasonable accuracy (10%). From the behavior of the first-order perturbed wave functions we hope then to make qualitative predictions that will enable us to derive semi-empirical theoretical descriptions applicable to larger systems.

It would be very useful if we could relate the magnitude of the electric polarizability to the chemical structure of a molecule. Insofar as the properties of molecular crystals depend on the properties of the individual molecules, the size, shape and electric polarizabilities are the key properties in determining crystal properties such as crystal structure, charge transfer, energy transfer and conductivity. We feel therefore that the derivation of semi-empirical theories of molecular polarizabilities is worth pursuing because such a theory can be of great use in understanding how the properties of molecular crystals relate to the type of molecules they contain.

Progress: Our research during the year 1974-75 has been proceeding according to plan, we have partially implemented the goals that we described in our research proposal and we are continuing along the same lines.

We described a method for calculating molecular electric polarizabilities and we showed that this method is capable of predicting the polarizabilities of the hydrogen molecule and the hydrogen molecular ion with an accuracy of better than 5%, using relatively crude wave functions. We also showed how this method can be improved; by extending the calculations to the next step, the accuracy of the results should be considerably improved. This analysis, combined with the derivation of the magnitudes of the errors in a number of related analogous procedures has just been submitted for publication.

Guided by the above general considerations we have planned three different lines of research in the general area of polarizability calculations and we are pursuing these lines simultaneously. (1) We wish to expand the H_2 calculation so that it can be applied to larger molecules. In order to do this we must develop a computer program that produces one- and two-electron integrals over molecular orbitals. It seems that this program is close to

being operational and we plan to use it on the LiH molecule first. An interesting secondary result of this treatment would be an accurate value for the electric dipole moment according to our general considerations.

(2) It follows from our error analysis that highly accurate polarizabilities may be obtained by solving both the first-order and the second-order perturbation equations. We have solved the first-order equations for some small atoms and molecules and we are now working on the solutions of the corresponding second-order perturbation equations. Hopefully the accuracy of the results obtained in this fashion are comparable to the accuracy of experimental values. These calculations are useful to have information about the magnitudes of the errors in the calculations described in (1).

(3) Our ultimate goal is to derive a semi-empirical theory of the polarizabilities of all types of molecules, comparable to our successful semi-empirical description of molecular diamagnetic susceptibilities. A difficulty here is the scarcity of reliable experimental results to use as a starting point for our discussion. Also, we would like to have some information available about the form of the first-order perturbed wave functions, we hope to derive this information for the calculations described in (1) on diatomics. Nevertheless we have begun to consider the trends in the polarizabilities of saturated hydrocarbons as a first step.

It is interesting that the various variation-perturbation methods that we have developed and analyzed are quite general and that they are not limited to electric perturbations only. In fact they can be used for calculating any first- or second-order molecular property. We have used the procedure for calculating the rotational magnetic moment of the hydrogen molecule and we are now engaged in solving the second-order perturbation equation in order to get a more accurate result. If we combine this with our planned calculation of the expectation value of $\langle \Sigma r^2 \rangle$ then we should obtain a value of the diamagnetic susceptibility that is more accurate than the available experimental result.

Publications:

Corsaro, F. A., Solenberger, F. R. and Hameka, H. F., "A Variational Perturbation Treatment of the Hydrogen Molecular-Ion Using the Green Function Method on the United Atom", Intl. J. of Quantum Chem. 8, 319 (1974)

Hall, W. R. and Hameka, H. F., Erratum: "Second-Order Effect of Spin-Orbit Coupling on the Angular Dependence of the Zero-Field Splitting in CH_2" [J. Chem. Phys. 58, 226 (1973)] J. Chem. Phys. 60, 4104 (1974)

Hameka, H. F., Quantum Theory of the Chemical Bond, Hafner Press, N. Y. (1975)

Kim, H-W. and Hameka, H. F., "Calculation of the Rotational Magnetic Moment of the Hydrogen Molecule", Chem. Phys. Lett. (Accepted)

Svendsen, E. N. and Hameka, H. F., "Calculation of the Magneto-Optical Activity of the Hydrogen Molecule", Intl. J. of Quantum Chem. 8, 789 (1974)

Svendsen, E. N. and Hameka, H. F., "Calculation of Molecular Electric Polarizabilities and Dipole Moments. I. General Theory and Application to the Hydrogen Molecule", J. Chem. Phys. 62, 2760 (1975)

Svendsen, E. N. and Hameka, H. F., "Effect of the Rotational Motion of Molecules on Their Optical and Their Magneto-Optical Activity", Intl. J. of Quantum Chem. (Accepted)

Svendsen, E. N. and Hameka, H. F., "On the Perturbation of Molecular Eigenfunctions by a Magnetic Field", Physica 74, 625 (1974)

4. Studies of Highly Conducting Organic and Polymeric Solids

A. J. Heeger, Professor of Physics
A. F. Garito, Associate Professor of Physics

Postdoctoral Fellows: A. A. Bright
C. Chiang
S. K. Khanna
E. F. Rybaczewski

Research Assistants: M. J. Cohen
L. B. Coleman
W. J. Gunning
J. C. Scott
L. S. Smith
R. Spal
T. S. Wei

Support: NSF-MRL
ARPA
IBM
NSF

Objective and Approach: Our objective is to develop a new class of materials composed of organic molecules with the eventual goal of technologically utilizing these materials for their electronic properties. The reason for the interest in these materials is the attractive feature that they are chemically synthesized from flat planar molecules which lead to anisotropic structures and pseudo one-dimensional electronic properties. We have successfully synthesized organic metals characterized by excess conductivity resulting from superconductive phenomena in one-dimensional conductors in the fluctuation regime. The work is interdisciplinary and involves a back-and-forth interplay between organic synthesis and broad-based experimental and theoretical physical studies. The overall goal is to create solid state materials with a desired bulk property by preliminary design of constituent molecules. Our efforts are expanding into inorganic compounds where the specific techniques of synthetic chemistry are required to achieve the desired novel structures and oxidation states.

Progress:

I. Organic Metals: TTF-TCNQ and Related Salts

The achievement of the metallic state and the observation of phenomena related to superconductivity in the class of organic solids known as charge transfer salts has continued to attract considerable interest, particularly TTF-TCNQ and related one-dimensional systems.

The pseudo-one-dimensionality of TTF-TCNQ has been established experimentally by a variety of measurements, where anisotropies of order $10^3 : 1$ have been observed in transport, dielectric, and optical properties. Early experimental studies of TTF-TCNQ and related systems centered on the DC conductivity. It is now generally agreed that the intrinsic conductivity at 58 K exceeds 10^4 $(\Omega\,\mathrm{cm})^{-1}$, and there is evidence that the peak value exceeds 10^5 $(\Omega\,\mathrm{cm})^{-1}$ undistorted by anisotropy-related effects. The sensitivity of the one-dimensional conductor to impurities and defects has been established, so that these values may only be lower bounds.

The studies of the electrical transport in TTF-TCNQ have been extended from dc through optical frequencies to provide a broader picture of the phenomena involved. The results for the frequency dependent conductivity, $\sigma_1(\omega)$, along the principal conducting axis of TTF-TCNQ can be summarized as follows:

-- Zero frequency (dc). The conductivity is approximately 10^3 $(\Omega\mathrm{cm})^{-1}$ at room temperature, increasing to values exceeding 10^4 - 10^5 $(\Omega\mathrm{cm})^{-1}$ near 58 K.

-- Microwave frequency (10^{10} GHz). The conductivity is approximately 10^3 $(\Omega\mathrm{cm})^{-1}$ at room temperature, increasing to values in the range 10^4 - 10^5 $(\Omega\mathrm{cm})^{-1}$ near 58 K. At both dc and microwave frequencies it appears likely that the peak conductivities are defect limited.

-- Infrared frequencies. There is an energy gap with magnitude $\hbar\omega_g \simeq 0.14$ eV above which the single-particle conductivity is Drude-like with a plasma frequency of $\hbar\omega_p \simeq 1.2$ eV.

The existence of a gap in the electronic excitation spectrum of TTF-TCNQ is of central importance to understanding the origin of the remarkable transport properties of this organic metal. The energy gap in the infrared, together with the relatively large dc and microwave conductivities, imply a correlated many-body state in which the low frequency conductivity results from a collective mode.

Very recently the existence of the Peierls distortion has been confirmed with x-ray studies carried out in a collaborative study between the Penn group and Dr. R. Comes and co-workers at Orsay. The superlattice has been observed at low temperatures with the dimensions of the superlattice unit cell being 2a x 3.7b x 2c. The fact that the superlattice period along b is evidently incommensurate with the underlying lattice is particularly important in that it implies that the distortion is driven by the soft $2k_F$ phonons and above 58 K, is the source of the high dc conductivity, the energy gap, and the overall features seen in $\sigma_1(\omega)$ and $\epsilon_1(\omega)$. As the temperature increases the superlattice Bragg peaks broaden into one-dimensional diffuse scattering streaks indicative of the Peierls-Fröhlich state in the fluctuation regime.

The existence of an incommensurate superlattice satisfies one essential condition for the Fröhlich type mechanism.

In summary the Peierls distortion has been demonstrated in TTF-TCNQ. The associated electronic optical, infrared, and magnetic data indicate that above 58 K, TTF-TCNQ has the properties of a one-dimensional superconductor in the fluctuation regime with a mean field scale temperature of order 400 K.

II. Polymeric Sulfur Nitride, $(SN)_x$: The First Metallic Polymer

The achievement of fully oriented epitaxial thin films of the electrically conducting metallic covalent polymer $(SN)_x$, polymeric sulfur nitride, was a focal point of the work on this inorganic polymer. This represents the first reported case of fully oriented epitaxial growth of thin films of any polymer. That this was possible for the metallic polymer $(SN)_x$ is of particular significance because of the anisotropic optical and electronic properties of this system.

Highly reflective golden thin films of $(SN)_x$ can be grown on glass or polymer substrates by direct sublimation of $(SN)_x$ crystals. The resulting films have the same crystal structure as the parent crystals and have similar electronic and optical properties. Optically reflective films have been grown on a variety of substrates. On glass substrates, polycrystalline films grow preferentially oriented with the mean plane $(\bar{1}02)$ of the $(SN)_x$ polymer chains parallel to the substrate surface. Complete epitaxial growth with $(SN)_x$ polymer chains oriented in a single direction within the plane is found for example, on teflon, mylar, and polyethylene substrates.

The anisotropic optical and electronic properties of the $(SN)_x$ oriented films are of potential technological use. The techniques developed in the LRSM allow $(SN)_x$-plastic substrate composites to be fabricated in order to explore particular mechanical, electrical, or optical features of the composites. For example, the large optical anisotropy of the oriented epitaxial films suggests the possibility of useful applications in integrated optical systems.

X-ray studies of $(SN)_x$ and of the parent molecular crystal S_2N_2 have been carried out. The results provide important information on the crystal structure of $(SN)_x$ and provide insight into the remarkable solid state polymerization process. $(SN)_x$ crystallizes in a monoclinic system (space group $P2_1/_C$) of one-dimensional polymer chains of alternate SN units along the crystallographic b-axis. The SN units are covalently bound with bond lengths of 1.60 and 1.62 Å, forming a flat $(SN)_x$ chain.

The interchain distance between two sulfur atoms on adjacent chains in the [201] direction is much shorter than van der Waals distances, implying

significant interchain coupling. In contrast, in the opposite [101̄] direction *the interchain S --- S distances are nearly identical to van der Waals distances* observed in many sulfur containing compounds. However, the N ... N distances are shorter in this direction.

We have measured the optical reflectance of polycrystalline films partially oriented on glass and the polarized reflectance of epitaxial films on plastic substrates as well as single crystals of $(SN)_x$ from the ultraviolet to the far infrared. The striking feature of the polarized data is the contrast with the polarized reflectance of electronically one-dimensional materials such as TTF-TCNQ and $K_cPt(CN)_4Br_{0.3} \cdot 3H_2O$. Such materials exhibit extreme optical anisotropy over the entire frequency range, where metallic reflectance is observed parallel to the principal conducting axis and relatively low reflectance in the perpendicular direction characteristic of an insulator. $(SN)_x$ does not exhibit the same extreme anisotropy over the full frequency range; in the parallel polarization, there is a well-defined plasma edge and minimum near 2.2×10^3 cm^{-1} and a relatively high, Drude-like metallic reflectance in the infrared. In the perpendicular polarization, $(SN)_x$ exhibits optical properties like those of a poor metal. The reflectance appears Drude-like with the characteristic increase in reflectance at low frequencies, but the relatively low value of the reflectance is indicative of a very high scattering rate.

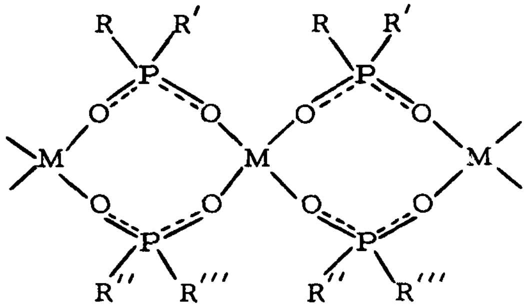
Studies of the transport properties, electrical conductivity and thermoelectric power indicate that $(SN)_x$ remains metallic over the entire temperature range below room temperature. The low temperature conductivity is defect limited. For material with fewer defects and impurities, the data show that samples having the highest room temperature conductivity exhibit the highest normalized peak conductivity at the lowest temperature and the highest conductivity at 4.2 K.

The superconductivity of $(SN)_x$ reported by the IBM (San Jose) group has been confirmed through collaborative studies with Prof. R. Pohl (Cornell) of heat capacity and Dr. R. Soulen (NBS) of resistivity at temperatures down to 0.1 K.

Current solid state studies are addressing the central question of the actual dimensionality of the electronic properties of $(SN)_x$. Although the chain-like structure suggests a one-dimensional electronic system, detailed studies show that substantial coupling takes place between $(SN)_x$ chains. The results indicate $(SN)_x$ should not be considered as strictly one-dimensional but rather should be approached from the point of view of an anisotropic solid with a two, or possibly, three dimensional electronic band structure.

III. Magnetic Transition Metal Polymers: The Role of Structural Disorder

The poly (metal phosphinates) represent an interesting series of inorganic coordination polymers whose solid state properties have been almost completely ignored. They are versatile materials capable of a variety of structures, crystalline modifications and physical properties. The polymeric nature of these compounds comes from the ability of the phosphinate anions to bridge between metal centers. Studies of these magnetic polymers are being carried out by Profs. A. F. Garito and A. J. Heeger in collaboration with Pierro Nannelli and H. D. Gillman (of the Pennwalt Corp.).



General structure of poly-metal-phosphinates. R, R$'$, R$''$, R$'''$ are alkyl groups or a phenyl group and may be the same or different. M is a metal, the oxidation state of which determines the number of phosphinate bridges.

Magnetic measurements have been reported for three poly-chromium-phosphinates. The results imply that these transition metal polymers comprise a class of one-dimensional antiferromagnetic chains with $J/k \sim 3K$ and with a varying degree of crystallinity. Structural disorder is found to limit the range of spin correlations and, in the extreme case, prohibits extended short range order.

The long range interest in these new materials arises since the metal ion can be of a transition series and therefore a magnetic site in the polymer chain. Since magnetic susceptibility measurements show that the spins are in general antiferromagnetically coupled, there is a possibility of varying the strength of this exchange interaction by substituting different R groups in the phosphinate (-OPRR$'$O-) bridges. This initial study shows that the magnetic properties of these polymers can be understood in traditional terms, and that they can be used (in conjunction with other techniques) as a probe of the microscopic structure of these transition metal polymers.

Publications:

Barmatz, M., Testardi, L. R., Garito, A. F. and Heeger, A. J., "Elastic Properties of One-Dimensional Compounds", Solid State Commun. 15, 1299 (1974)

Bright, A. A., Chaikin, P. M. and McGhie, A. R., "Photoconductivity and Small Polaron Effects in TCNQ", Phys. Rev. 10, 3560 (1974)

Bright, A. A., Cohen, M. J., Garito, A. F., Heeger, A. J., Mikulski, C. M. and MacDiarmid, A. G., "Epitaxial Crystalline Films of the Metallic Polymer: $(SN)_x$", Appl. Phys. Lett. 26, 612 (1975)

Bright, A. A., Cohen, M. J., Garito, A. F., Heeger, A. J., Mikulski, C. M., Russo, P. J. and MacDiarmid, A. G., "Optical Reflectance of Polymeric Sulfur Nitride Films from the Ultraviolet to the Infrared", Phys. Rev. Lett. 34, 206 (1975)

Bright, A. A., Garito, A. F., and Heeger, A. J., "Optical Conductivity Studies in a One-Dimensional Organic Metal: Tetrathiofulvalene Tetracyanoquinodimethan (TTF)(TCNQ)", Phys. Rev. B 10, 1328 (1974)

Cohen, M. J., Coleman, L. B., Garito, A. F. and Heeger, A. J., "Electrical Conductivity of Tetrathiofulvalinium Tetracyanoquinodimethan (TTF)(TCNQ)", Phys. Rev. B 10, 1298 (1974)

Cohen, M., Khanna, S. K., Gunning, W. J., Garito, A. F. and Heeger, A. J., "Theory of Microwave Losses of One-Dimensional Conductors in the Skin Effect Regime: Application to TTF-TCNQ", Solid State Commun. 17, 367 (1975)

Coleman, L. B., Yamagishi, F. G., Garito, A. F., Heeger, A. J., Dahm, D. J., Miles, M. G. and Wilson, J. D., "TTF-TCNQ: Evidence of Alternating Chains in a Derivative Salt", Phys. Lett. 51A, 412 (1975)

Garito, A. F. and Heeger, A. J., "The Design and Synthesis of Organic Metals", Accts. Chem. Res. 7, 232 (1974)

Garito, A. F. and Heeger, A. J., "Tetrathiofulvalinium Tetracyanoquinodimethan (TTF)(TCNQ): A One-Dimensional Organic Metal", Nobel Symposium No. 24, Collective Properties of Physical Systems, Ed., S. Lundquist (Nobel Press 1974)

Heeger, A. J. and Garito, A. F., "The Electronic Properties of TTF-TCNQ", Low-Dimensional Cooperative Phenomena, Ed., H. J. Keller, Plenum Publishing Corporation 1975, p. 89

Jacobsen, C. S., Tanner, D. B., Garito, A. F. and Heeger, A. J., "Single-Crystal Reflectance Studies of Tetrathiafulvalene Tetracyanoquinodimethane", Phys. Rev. Lett. 33, 1559 (1974)

Khanna, S. K., Bright, A. A., Garito, A. F. and Heeger, A. J., "Evidence of Strong Coulomb Interactions in Alkali-TCNQ Salts", Phys. Rev. B 10, 2139 (1974)

Khanna, S. K., Ehrenfreund, E., Garito, A. F., and Heeger, A. J., "Microwave Properties of High Purity Tetrathiofulvalene-Tetracyanoquinodimethan (TTF-TCNQ)", Phys. Rev. B 10, 2205 (1974)

Khanna, S. K., Garito, A. F., Heeger, A. J. and Jaklevic, R. C., "Anisotropic Dielectric Constant of TTF-TCNQ Observed by Dielectric Resonance", Solid State Commun. 16, 667 (1975)

Kwak, J. F., Chaikin, P. M., Russel, A. A., Garito, A. F. and Heeger, A. J., "Anisotropic Thermopower of TTF-TCNQ", Solid State Commun. (Accepted)

MacDiarmid, A. G., Mikulski, C. M., Saran, M. S., Russo, P. J., Cohen, M. J., Bright, A. A., Garito, A. F. and Heeger, A. J., "Synthesis and Selected Properties of Polymeric Sulfur Nitride, $(SN)_x$", Proc. of Symposium on Inorganic Solids with Unusual Electronic Properties (Accepted)

McGhie, A. R., Garito, A. F. and Heeger, A. J., "A Gradient Sublimer for Purification and Crystal Growth of Thermally Unstable Organic Compounds", J. Cryst. Growth 22, 295 (1974)

Murgich, J., "Nuclear Quadrupole Resonance of ^{14}N in Cubic Tetracyanoethylene", Chem. Phys. Lett. 18, 420 (1974)

Murgich, J. and Pissanetzky, S., "Temperature Dependence of the ^{14}N Nuclear Quadrupole Resonance and the Observation of the Phase Transition in Cubic Tetracyanoethylene", J. Chem. Phys. 62, 92 (1975)

Rybaczewski, E. F., Garito, A. F., Heeger, A. J. and Ehrenfreund, E., "Nuclear Spin-Lattice Relaxation and Local Susceptibilities in Tetrathiafulvalene Tetracyanoquinodimethane", Phys. Rev. Lett. 34, 524 (1975)

Sandman, D. J. and Garito, A. F., "An Improved Synthetic Route to 11, 11, 12, 12-Tetracyanonaphtho-2, 6-quinodimethan (TNAP)", J. Org. Chem. 39, 1165 (1974)

Scott, J. C., Garito, A. F. and Heeger, A. J., "Magnetic Susceptibility Studies of Tetrathiofulvalene-Tetracyanoquinodimethan (TTF)(TCNQ) and Related Organic Metals", Phys. Rev. B 10, 3131 (1974)

Scott, J. C., Garito, A. F., Heeger, A. J., Nannelli, P. and Gillman, H. D., "The Magnetic Properties of Poly(Metal Phosphinates): The Effects of Structural Disorder on One-Dimensional Antiferromagnetic Chains", Phys. Rev. B 12, 356 (1975)

Tanner, D. B., Jacobsen, C. S., Garito, A. F. and Heeger, A. J., "Infrared Conductivity of (TTF)(TCNQ) Films", Phys. Rev. Lett. 32, 1301 (1974)

5. Optical Studies in Liquid Crystals and Magnetic Materials

J. T. Ho, Associate Professor of Physics (now at University of Houston)

Research Assistants: C-C. Huang
R. S. Pindak

Support: NSF-MRL
RC
U of P

Objective and Approach: This is an experimental investigation of physical properties near second-order or continuous phase transitions, an area of intense current interest because of the discovery of rather universal behavior among very different systems and because of recent major theoretical advances. Two systems under study at this time are liquid crystals and ferromagnets. Liquid crystals are organic compounds with elongated molecules which melt into a variety of anisotropic liquid phase before changing into the isotropic liquid. Phenomenological descriptions of the equilibrium and time-dependent properties of these phases have only recently been introduced, and measurements will be made for comparison with these theoretical predictions. Of particular interest are the regions of transition from one liquid-crystalline phase to another, some of which have been shown to be possibly continuous and formally analogous to (but experimentally more tangible than) the superconducting transition. The anisotropy and fluctuations in liquid crystals lead to pronounced optical and light scattering phenomena, which will be exploited in the measurements. Similar techniques will be used to study the properties near the critical point of magnetic crystals which exhibit large magneto-optical effects. Such studies will not only be of importance in understanding the structure of matter but will also be of value to potential applications of these for optical display, memory, modulation and other devices.

Progress: We have used the dynamic Freedericksz-deformation method to measure in detail the temperature dependence of the twist viscosity in N-p-cyanobenzylidene-p-octyloxyaniline (CBOOA) near the nematic-smectic-A transition. We have demonstrated that the intrinsic contribution can be determined independently by extrapolating data on doped samples. Our analysis shows the twist viscosity to diverge with a critical exponent 0.37 ± 0.05, in agreement with dynamic scaling predictions.

Depolarized light scattering has been used to measure the splay and bend elastic constants in nematic CBOOA near the smectic A phase. The splay elastic constant shows no pretransitional anomaly. The bend elastic constant diverges with a critical exponent 0.68 ± 0.02. These results are in accordance with the superfluid analogy of the nematic-smectic-A transition suggested by de Gennes.

The static magnetic properties of EuO near its Curie point has been measured using the Faraday effect. Comparison with magnetometer measurements reveal a small non-linear term in the relation between rotation and magnetization. With this correction, our results yield the critical exponents $\beta = 0.370 \pm 0.006$ and $\gamma = 1.30 \pm 0.02$. All our data can be scaled using these two exponents and are also describable using two different parametric equations of state.

Publications:

Huang, C. C., Pindak, R. S., Flanders, P. J. and Ho, J. T., "Dynamics of Freedericksz Deformation near a Nematic-Smectic-A Transition", Phys. Rev. Lett. 33, 400 (1974)

Huang, C. C., Pindak, R. S. and Ho, J. T., "Birefringence and Order Parameter in Nematic N-p-Cyanobenzylidene-p-Octyloxyaniline", J. Phys. (Paris) 35, L-185 (1974)

6. Electronic Structure and Relaxation Processes in Molecular Crystals

R. M. Hochstrasser, Blanchard Professor of Chemistry

Postdoctoral Fellow:	R. G. Bray
Research Assistants:	J. M. Friedman D. S. King C. M. Klimcak F. A. Novak C. A. Nyi H-N. Sung
Support:	NSF-MRL NIH NSF AROD USA U of P

Objective and Approach: This work seeks to explore novel properties of molecular solids and to relate the physical and chemical properties of molecular crystals and aggregates of organic molecules to the structures of the component molecules. We are particularly interested in the excited states of molecular crystals including: the interactions leading to exciton bands; the mechanisms of energy transfer throughout the crystal; the mechanisms of various deactivation processes including isotopically selective photochemical processes in the solid and their topological features; the electronic properties of molecular materials such as electric moments, polarizabilities, non-linear polarizabilities; and the mechanisms of photoexcitation in molecular solids including the interplay between inelastic light scattering and relaxation processes in the condensed phase.

When molecules in a solid are excited by light they may undergo many different possible processes. The energy may be utilized to initiate a chemical process, or it may be rapidly transferred away to other sites, or rapidly transformed into vibrational energy and thence to lattice phonons. The processes that occur are determined by the nature of the state excited and its interactions with the surroundings. Thus a complete understanding of processes in model systems includes studies of molecular properties, of chemical dynamics and the characterization of the states of molecules and molecular crystals.

A wide range of techniques are employed or developed for these studies, including: low temperature high resolution spectroscopy in association

with high magnetic and electric field effects; Resonance Raman spectroscopy; EPR, ENDOR and various other double resonance techniques; laser induced two-photon spectroscopy to high resolution; mode-locked lasers and pulsed tunable dye lasers to explore the picosecond time domain, and the detailed responses of molecules and molecular crystals to intense light fields.

Progress:

1. By measuring the shift of an optical transition in an electric field we have obtained results that will lead to reliable values for the polarizability anisotropy of the anthracene molecule in its first excited state. This is the first direct measurement of the polarizability components for an excited molecule in an ordered environment. (Continuing)

2. Following our discovery that the 1, 4-dibromonaphthalene crystal forms effectively one-dimensional exciton bands we have successfully measured the density of triplet exciton states using a novel band-to-band transition technique. The density of states is double humped - as expected - but appears perturbed perhaps due to inter-band coupling. We have succeeded in modulating the luminescence of this system using an electric field to improve the one-dimensional character of the band. (Continuing)

3. We have made a direct measurement of the modification of the charge distribution of one molecule (naphthalene) caused by a nearest neighbor (~ 5 Å) polar molecule (quinoxaline). The measured induced moment magnitude and direction could not be rationalized on any elementary grounds.

4. We have made for the first time direct measurements of energy and electron transfer between neighboring molecules. This was done both by arranging to have the excited donor and ground state acceptor molecules in van der Waals contact, and by connecting them together through 'inert' chemical linkages like $-CH_2-$ groups. For the case benzophenone to naphthalene we measured directly a transfer time of 2×10^{-11} sec. using mode-locked laser pulses.

5. We have made an approximate theoretical description of the relationship between the temporal and spectral widths of light pulses and the processes of Raman scattering and resonance fluorescence. We find important formulae describing the light scattering from discrete states imbedded in continua. This work explained important new experiments by Bell Telephone Labs. researchers, and also resonance scattering experiments done by ourselves.

6. We have successfully performed for the first time a laser induced isotope separation in the solid state, producing $HC^{13}N^{14}$ from the photolysis of s-tetrazine at 1.6 K. The enrichment was close to 100%.

7. We have developed a technique for measuring optical spectra in the range 380 - 850 mm during a 3 ps interval.

Publications:

Anderson, R. W., Jr., Hochstrasser, R. M., Lutz, H. and Scott, G. W., "Direct Measurements of Energy Transfer between Triplet States of Molecules in Liquids Using Picosecond Pulses", J. Chem. Phys. 61, 7, 2500 (1974)

Anderson, R. W., Jr., Hochstrasser, R. M., Lutz, H. and Scott, G. W., "Direct Measurements of Internal Conversion between Excited Electronic States of a Molecule in the Condensed Phase", Chem. Phys. Lett. 32, 204 (1975)

Anderson, R. W., Hochstrasser, R. M., Lutz, H. and Scott, G. W., "Measurements of Intersystem Crossing Kinetics Using 3545 Å Picosecond Pulses: Nitronaphthalenes and Benzophenone", Chem. Phys. Lett. 28, 153 (1974)

Bray, R. G., Hochstrasser, R. M. and Sung, H. N., "Two-Photon Excitation Spectra of Molecular Gases: New Results for Benzene and Nitric Oxide", Chem. Phys. Lett. 33, 1 (1975)

Bray, R. G., Hochstrasser, R. M., and Wessel, J. E., "Continuously Tunable Two-Photon Excitation of Individual Rotational Levels of the $A^2\Sigma^+$ State of Nitric Oxide", Chem. Phys. Lett. 27, 2, 167 (1974)

Friedman, J. M. and Hochstrasser, R. M., "Interference Effects in Resonance Raman Spectroscopy", Chem. Phys. Lett. 32, 414 (1975)

Friedman, J. M. and Hochstrasser, R. M., "Moderately High Resolution Fluorescence Spectrum of the $S_1 \rightarrow S_0$ Transition of Azulene", Chem. Phys. 6, 145 (1974)

Friedman, J. M. and Hochstrasser, R. M., "Time Dependence of the Resonant and Near Resonant Photon Molecular Interactions", Chem. Phys. 6, 155 (1974)

Hochstrasser, R. M., "Some Aspects of Energy Transfer in the Organic Solid State", in Energy Transfer, Eds., Levine and Jortner, Academic Press (1975) (Accepted)

Hochstrasser, R. M., "Triplet Excitons", MTP Int. Rev. Sci., Eds., Ramsay and Buckingham, Butterworth (1975) (Accepted)

Hochstrasser, R. M. and King, D. S., "Absorption, Fluorescence and Phosphorescence Spectra of the Singlet and Triplet States of s-Tetrazine in the Crystal and in Mixed Crystals at Low Temperatures", Chem. Phys. 5, 439 (1974)

Hochstrasser, R. M., Li, T-Y., Sung, H-N., Wessel, J. and Zewail, A. H., "Experimental Studies of Triplet Exciton Bands of Molecular Crystals", Pure Appl. Chem. 37, 85 (1974)

Hochstrasser, R. M. and Wessel, J. E., "Time Resolved Fluorescence of Anthracene in Mixed Crystals at 2 K", Chem. Phys. Lett. 6, 19 (1974)

Hochstrasser, R. M. and Zewail, A. H., "Optical and Magnetic Resonance Spectra of Linear Chain Excitons", Chem. Phys. 4, 142 (1974)

Friedman, J. M. and Hochstrasser, R. M., "The Use of Fluorescence Quenchers in Resonance Raman Spectroscopy", Chem. Phys. Lett. 33, 225 (1975)

7. Synthesis and Study of Organometallic and Polymeric Metallic Conductors

A. G. MacDiarmid, Professor of Chemistry

Postdoctoral Fellows: C. M. Mikulski
P. J. Russo
M. S. Saran

Support: NSF-MRL
NSF
ONR
NATO

Objective and Approach: The objective of this research is to synthesize and study new inorganic and organometallic materials which might exhibit, or might be expected to exhibit, novel electrical or magnetic properties. It is believed that, for the continued active growth of materials science, it is necessary to have a vigorous program involving the synthesis of new types of substances. Exciting, important, "quantum-jumps" occur when new substances with unexpected, scientifically or technologically important properties are discovered.

The broad objective of this investigation is to synthesize and study new chemical compounds which behave as metals. Of particular, but not exclusive, interest are polymers which are metals, even though they contain no metal atoms. The first example of such a polymer, the remarkable compound, polymeric sulfur nitride $(SN)_x$, was synthesized for the first time in the form of pure golden crystals in this laboratory during the past year. It is believed $(SN)_x$ may be the forerunner of a whole new class of inorganic "polymeric metals" based on diatomic neutral, cationic or anionic monomeric units containing one unpaired electron, isoelectronic with $(SN)_x$. The synthesis and study of such compounds will be undertaken.

Progress: During the past twelve months analytically pure crystals of polymeric sulfur nitride $(SN)_x$ have been synthesized in this laboratory. This was the first time this synthesis had ever been accomplished in any laboratory - academic, governmental or industrial. During early stages of the research it frequently took several weeks to make even small crystals of $(SN)_x$ and, often, these were impure, since the synthetic methods were unreliable. The synthesis of $(SN)_x$ is now very much better understood and up to half a gram of pure golden crystals of $(SN)_x$ can now be reliably and reproducibly synthesized in four to five days. A reliable method of production of pure $(SN)_x$ was, of course, indispensable, before a thorough investigation of its physical and chemical properties could be undertaken.

A completely new method for making $(SN)_x$ has been worked out. Pure S_2N_2 is first prepared (by passing S_4N_4 vapor over hot silver wool).

Crystals of colorless S_2N_2 are then grown at 0°C and are permitted to polymerize in the solid state at room temperature to give crystals of $(SN)_x$ which are pseudomorphic with the S_2N_2 crystals from which they are derived. The S_2N_2 crystals pass through a blue-black paramagnetic form as they polymerize to $(SN)_x$, but the final pure material is diamagnetic.

Preliminary experiments show that $(SN)_x$ crystals are not attacked during one week at room temperature by: (i) oxygen at one atmosphere pressure; (ii) water vapor at 5 mm pressure; (iii) oxygen at one atmosphere pressure saturated with water vapor. $(SN)_x$ is not attacked by water during one day at room temperature.

Crystalline $(SN)_x$ can be sublimed in vacuo at 130°-140°C with constant pumping to give golden cohesive films of epitaxial $(SN)_x$ on various substrates* if the condensing surface is approximately 25°C. If the condensing surface is at liquid nitrogen temperature S_2N_2 is collected together with an unstable dark red compound, possibly monomeric NS, which rapidly changes to S_2N_2 and $(SN)_x$ at 0°C. The formation of S_2N_2 (and possibly NS) when $(SN)_x$ is heated is confirmed by mass spectral studies. Crystalline $(SN)_x$ therefore sublimes by a process involving the depolymerization of $(SN)_x$ to S_2N_2 and possibly NS, viz.

$$
\begin{array}{cccc}
(SN)_x \xrightarrow{140^\circ} & S_2N_2\,(\text{vapor}) & + & NS\,(\text{vapor}) \\
 & \downarrow & & \downarrow \\
 & S_2N_2 & & (SN)_x \\
 & \text{crystals} & & \text{films}
\end{array}
$$

It is believed that cohesive $(SN)_x$ films are formed only from the dark red unstable compound, which is very likely NS. When $(SN)_x$ is heated in a sealed tube at 140°, it slowly decomposes to nitrogen and sulfur, presumably due to the thermal decomposition of the S_2N_2 which is first formed from the $(SN)_x$ at this temperature. When the $(SN)_x$ is heated under nitrogen at a heating rate of 1°C/minute, it decomposes very rapidly at approximately 210°C.

In order to attempt to understand the solid state polymerization of S_2N_2 to $(SN)_x$, a single crystal X-ray structural study of S_2N_2 was performed at -130°.** Disulfur dinitride, S_2N_2 (space group $P2_{1/C}$), has the cell

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* An extensive study of the electrical and optical properties of $(SN)_x$ and the formation of epitaxial films of $(SN)_x$ has been carried out in collaboration with Drs. A. F. Garito and A. J. Heeger. This work has been undertaken primarily by these groups and is described in their progress reports.

** Performed by the Molecular Structure Corp., College Station, Texas 77840

constants (R = 0.03): a = 4.485(2), b = 3.767(1), c = 8.452(3) Å; β = 106.43(4)° with ρ_c = 2.23 g/cm^3 with two S_2N_2 molecules per unit cell. The molecule is square planar with essentially equal S-N bond lengths [1.657(1) and 1.651(1)]. The S-N-S angle is 90.4(1)° and the N-S-N angle is 89.6(1)°. A single crystal X-ray structural study of $(SN)_x$ has also been performed* both at room temperature and at -130°C. Very little structural change is observed between these two temperatures. The $(SN)_x$ crystals are composed of an ordered array of parallel $(SN)_x$ fibers which consist of an almost planar chain of alternating sulfur and nitrogen atoms and are pseudomorphs of, and have the same space group ($P2_{1/C}$) as the S_2N_2 crystals from which they are derived. The cell constants are a = 4.153(6); b = 4.439(5) and c = 7.637(12) Å; β = 109.7(1)° with ρ_c = 2.30 g/cm^3 for four SN units per unit cell. The refined structure (R = 0.11) shows nearly equal S-N bond lengths, 1.593(5) and 1.628(7) Å. The S-N-S angle is 119.9(4) and the N-S-N angle is 106.2(2)°.

It appears possible that $(SN)_x$ may be the forerunner of a whole new class of covalent polymers which are metals, even though they contain no metal atoms. Very considerable emphasis is now being placed on synthesizing new polymers of this type while at the same time studying the mechanism of the polymerization of S_2N_2 to $(SN)_x$ and the chemical properties of $(SN)_x$.

Publications:

Bright, A. A., Cohen, M. J., Garito, A. F., Heeger, A. J., Mikulski, C. M. and MacDiarmid, A. G., "Epitaxial Crystalline Films of the Metallic Polymer: $(SN)_x$", Appl. Phys. Lett. 26, 612 (1975)

Bright, A. A., Cohen, M. J., Garito, A. F., Heeger, A. J., Mikulski, C. M., Russo, P. J. and MacDiarmid, A. G., "Optical Reflectance of Polymeric Sulfur Nitride Films from the Ultraviolet to the Infrared", Phys. Rev. Lett. 34, 206 (1975)

Mikulski, C. M., Russo, P. J., Saran, M. S., Garito, A. F., Heeger, A. J. and MacDiarmid, A. G., "Synthesis and Structure of the Polymeric Metal, $(SN)_x$, and Its Precursor, S_2N_2", Chem. Commun. 476 (1975)

Mikulski, C. M., Saran, M. S., Russo, P. J., Cohen, M. J., Bright, A. A., Garito, A. F. and Heeger, A. J., "Synthesis and Selected Properties of Polymeric Sulfur Nitride, $(SN)_x$" in Advances in Chemistry, Ed., R. B. King, Am. Chem. Soc. (Accepted)

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* Performed by the Molecular Structure Corp., College Station, Texas 77840

8. Synthesis and Studies of Mixed Valence Compounds

L. G. Sneddon, Assistant Professor of Chemistry

Research Assistants: M. Freeman
J. S. Plotkin

Support: NSF-MRL
RC

Objective and Approach: Mixed valence inorganic compounds have been shown to have a number of unique physical and chemical properties. These properties range from color, magnetism and solid state conductivity to chemical reactivity. Recently mixed valence organometallic compounds have received an increased amount of attention. Most of the work has centered around biferrocenes, bis-fulvalene iron and cobalt complexes and ferrocene polymers. In every case, once these compounds were converted to the mixed valence state, a dramatic increase in the electrical conductivity was observed. By combining the synthetic possibilities of organometallic chemistry with the concepts developed in solid state physics, we are attempting to synthesize new mixed valence organometallic compounds which may exhibit a variety of electrical properties (semiconducting, conducting and superconducting).

Progress:

1. In the gas phase cyclopentadienyl thallium(I), C_5H_5Tl, and cyclopentadienyl indium(I), C_5H_5In, consist of discrete molecules having five-fold symmetry, the metal atoms lying over the rings to form a half sandwich structure. In the solid state, however, both compounds have been shown to be linear zig-zag polymers of alternating metal and cyclopentadienyl ions. For C_5H_5In the metal to ring distance is 3.19 Å and the metal-metal distance is 3.99 Å, which is small enough to allow the possibility of some electronic interaction. Partial oxidation of a pseudo-one dimensional stack such as TlC_5H_5, by electron acceptors such as TCNE or TCNQ, could lead to a Tl(I)-Tl(III) mixed valence polymer associated with stacks of TCNQ or TCNE anions.

We have recently discovered that when TCNE and TlC_5H_5 are mixed in the solid phase a golden-red material is produced which we believe is the mixed valence polymer. We have also been able to produce thin films of this material by co-subliming TCNE and TlC_5H_5 on to small glass plates. These films have a lustrous golden appearance and are highly reflective. We are presently preparing films and single crystals for solid state measurements. In addition we are investigating the reaction of TlC_5H_5 with other electron acceptors such as TCNQ.

2. The use of electron deficient cage systems as ligands to form metallocene-like transition metal complexes has developed into a significant

new branch of organometallic chemistry. These cage systems have many direct organic analogs, but the variety of ligands, as well as the novel structural features encountered, have no parallel in conventional organometallic chemistry. Of particular interest is the ability of these ligands to form multi-metal layered compounds. We are presently employing a wide variety of synthetic methods in an attempt to produce new small cage ligands which should be capable of forming layered complexes. The properties and chemistry of these layered compounds will be studied with a view toward converting these compounds to the mixed valence state. This may be accomplished electrochemically or by the reaction of the complex with a suitable electron donor such as tetrathiofulvalene (TTF). Preliminary work has already started on the reaction of TTF with the triply decked compound $(\pi\text{-}2,3\text{-}C_2B_3H_5)Co_2(\pi\text{-}C_5H_5)_2$.

3. The closo-carborane cage compounds have also proven to be excellent electron acceptors, and so in addition to the above studies involving metal complexes, a new project investigating the reaction of closo-carboranes with various electron donors such as TTF has been initiated. Initial results indicate that TTF does react with various carboranes and boranes in acetonitrile solution. The nature of the reaction has not been determined, but it is hoped that charge transfer salts will result. Work is continuing in this area.

Publications:

Greenwood, N. N., Savory, C. G., Grimes, R. N., Sneddon, L. G., Davison, A., Wreford, S., "Preparation of a Stable Ferraborane, $B_4H_8Fe(CO)_3$", Chem. Comm. 718 (1974)

Magee, C. P., Sneddon, L. G., Beer, D. C. and Grimes, R. N., "Bridge Insertion Reactions of the $2,3\text{-}C_2B_4H_5$ -Ion with Aluminum Gallium and transition Metal Reagents", J. of Orgmet. Chem. 86, 159 (1975)

Sneddon, L. G. and Lagow, R. J., "The Reaction of Lithium Vapor with Partially Halogenated Hydrocarbons", Chem. Commun. (Accepted)

9. Spectroscopic Studies of Molecular Relaxation in Condensed Media

M. R. Topp, Assistant Professor of Chemistry

Research Assistant: G. C. Orner

Support: NSF-MRL
NSF

Objective and Approach: Recent developments in laser techniques have provided the means for accurate analysis of molecular behavior, through experiments in time-resolved spectroscopy, flash-photolytic measurements of the rates of solvent-cage dominated photochemical reactions, and the direct investigation of the effects of high-intensity optical pulses on the physical properties of molecules and molecular aggregates.

Picosecond lasers constitute a potentially powerful tool for the investigation of primary processes following the interaction of light with matter, and thereby may be used to study molecular properties, in particular energy redistribution and dissipation. However, as it stands, the mode-locked laser oscillator is not particularly suitable for molecular dynamic studies. Although the pulse durations may be reliably less than 10^{-11} sec, the spectral frequency is often inappropriate, and the events initiated by such short pulses are too fast for direct, conventional electronic analysis.

It has been our primary initial aim to relieve ourselves of these limitations, principally by developing a reliable method for generation of high-intensity tunable ultraviolet picosecond pulses and, by using the principles of linear optics, to arrive at a new method for direct analogue photoelectric analysis of rapid events with pulse-duration-limited time-resolution.

Optical principles determine our time-resolution and our detection methods rely on optical double resonance spectroscopy, where we probe the change in spectral response of a particular system induced by an intense irradiation pulse. In this way, we may study the rate and extent of relaxation processes in condensed media, which depend critically on the nature of the medium, and on local dielectric conditions around a particular molecule. We may study directly the coupling of excitation energy to neighboring chromophores and thereby obtain unique information about the way in which excitation energy is transported through a molecular aggregate.

Progress:

Picosecond Pulse Dispersion and Photoelectric Analysis

There has been a recent controversy concerning the factors governing the dispersion of optical pulses in condensed media. This has led to misinterpretations of the results of important experiments. We have established an

accurate empirical correlation between linear group dispersion theory and the propagation of picosecond pulses in liquids (although non-linear optical effects result in some pulse distortion at extreme intensities). This has been possible as a result of the development in our laboratory of new, accurate techniques for picosecond time-resolution and intensity measurement.

However, perhaps more significant than this clarification has been our experimental confirmation that out of the difference between group and phase propagation of light there arises a spatial time-dispersion across the profile of a picosecond laser pulse. We have used this effect, together with photoelectric image-analysis techniques to design a simple, accurate method for direct analogue oscilloscope display of picosecond fluctuations in light intensity. This is the first time that this has been done in a simple manner without histogram time-segmentation. For monochromatic picosecond analysis this new method will probably replace similar methods presently in use in view of the hitherto unprecedented accuracy, sensitivity and time-resolution.

Apart from analytical considerations, the above technique introduces coherent pulse expansion, and thus essential laser properties are conserved. This is thus a valuable method for control of both pulse duration and shape, which should find widespread use in analysis and control of time-dependent non-linear optical phenomena, including self-focusing and stimulated scattering effects. We hope to use this for studies of saturation of inhomogenously broadened absorption and emission spectra.

Biphotonic Excitation of Low Quantum-Yield Fluorescence from Upper Singlet States

Fluorescence spectroscopy is one of the most sensitive and versatile methods for identification of molecular energy levels, and the laser is an ideal excitation source for detection of potentially fluorescent species. However, the observation of weak fluorescence is frequently impeded by the presence of high-intensity emission or scattered light, the former resulting from different energy levels in the same species, from impurities, or from other components in molecular aggregates.

We have used a new biphotonic method for unique excitation of low quantum-yield fluorescence to measure upper state fluorescence spectra in certain important organic dyes. Since the two irradiation frequencies lie below the range of the fluorescence spectrum, neither scattering nor impurity fluorescence is sufficiently intense to mask the spectrum. The intensity of excitation is actually higher in our experiments than for the direct (relatively weak, ultraviolet) irradiation process: The ground state species is initially depopulated by an intense pulse into the first excited state, and then this excited state is excited even more strongly by an intense infrared laser pulse into an upper excited state, from which fluorescence to the ground state is observed. These measurements, which yield valuable information

about the lifetime and electron distribution of upper states, form a natural complement to the direct, time-resolved picosecond studies.

Activation-Controlled Geminate Photochemical Reaction

The measurement of environmental effects on the rate of a translationally-restricted photochemical reaction provide a further valuable complement to our faster molecular energy-relaxation studies. In this study we have used our own techniques for nanosecond flash photolysis to measure excited state quenching by a photochemically-active environment. From the results we have been able to measure solvent cage correlation times, in addition to explaining the rate of an environmentally-controlled radiationless relaxation process in terms of the reversible formation of transient complexes in solid solution.

Such information is valuable not only in its own right but in view of the possibilities for laser-control of the outcome of chemical reactions by selective excitation in the appropriate solid environment.

Short-Range Molecular Interactions in Inhomogeneous Dielectric Media

It is well known that the fluorescence spectrum of a polar molecule in a polar medium is dependent on both the dielectric constant of the medium, and the viscosity. Measurements of time-resolved fluorescence spectral changes are valuable to the understanding of the interaction between the polar molecule and the induced dielectric inhomogeneity in the "cosphere". Here, picosecond time-resolved experiments are important for measurement of these parameters in low-viscosity systems.

However, we have also studied by simple fluorescence spectroscopy the dependence of fluorescence spectral position and shape on solvent composition, by observation of the non-stoichiometric dependence of the observed dielectric constant on the concentration of added polar solute to a substantially less polar solution of a polar dye. We are now in a position to calculate effective dielectric constants as experienced by probe molecules, which differ sharply from the bulk measurements, in exhibiting nanosecond time-dependence.

Calculations based on continued experiments in this area will be of considerable value in studies of dipole-induced dielectric relaxation, and more generally of encounter lifetimes and selective affinity in catalytic processes.

Publications:

Topp, M. R., "Activation-Controlled Hydrogen Abstraction by Benzophenone Triplet", Chem. Phys. Lett. 32, 144 (1975)

Topp, M. R., "Oscilloscope Display of Picosecond Fluctuations in Light Intensity", Opt. Comm. (Accepted)

Topp, M. R. and Orner, G. C., "Group Dispersion Effects in Picosecond Spectroscopy", Opt. Comm. 13, 276 (1975)

Topp, M. R. and Orner, G. C., "Group Dispersion Effects in Picosecond Spectroscopy: Frequency Dispersion", Chem. Phys. Lett. (Accepted)

10. The Determination of the Molecular Structures of Nucleic Acid Components and of Proteins by X-Ray Diffraction Techniques

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Postdoctoral Fellows: V. Belsky
G. J. Bunick
F. E. Scarbrough

Research Assistants: G. P. McKenna
H-S. Shieh

Support: NSF-MRL
NIGMS

Objective and Approach: The forces between molecules appear to be far more specific than has generally been appreciated. This is particularly true of hydrogen bonding interactions between heterocyclic molecules such as purines and pyrimidines. X-ray structural evidence that we have recently gathered suggests that the alterations in the electronic structures of such molecules that are caused by their interactions may be reflected in the structural patterns of their associations. We have investigated the nature of the interactions between adenine derivatives and uracil derivatives by the X-ray structural determination of a series of complexes in which the covalent structure of one or the other of these molecules is systematically varied. We are also investigating the structural effect of associating adenine with nicotinamide derivatives and with flavin derivatives in order to shed light on the role of adenine in the redox coenzymes NAD and FAD respectively. The information elucidated by the above sorts of X-ray investigations should contribute significantly to our understanding of how molecules associate.

A second major project that is underway is the X-ray structure determination of the yeast enzyme pyrophosphatase. The results of this study should lead to an understanding of the catalytic mechanism of this enzyme and increase our general knowledge of the forces that maintain the conformations of proteins.

Progress: We have solved the structures of several aderine · barbiturate type complexes. These include the complexes 9-ethyladenine · parabanic acid · oxaluric acid monohydrate, 9-ethyladenine · parabanic acid, and 8-bromo-9-ethyladenine · cyanuric acid. The st. ıcture of these complexes, when taken together with previous structural work, clearly demonstrate that in molecules such as barbiturates, which have several closely associated carbonyl groups, the hydrogen bond acceptor strength of the carbonyl groups is greatly attenuated. This is quite contrary to expectations deriving from the electrostatic theory of hydrogen bonding. Also during the past year we have been working on the crystal structures of the complexes

2, 6-diamino-9-ethylpurine · 5-acetyl-1, 5-dihydrolumiflavin, 9-ethyladenine · cyanuric acid, 2, 6-diamino-9-ethylpurine · 5, 5-diethylbarbituric acid and on the molecule 8-aza-ε-adenosine. These studies are in various stages of completion.

We have undertaken, in collaboration with Dr. David Porter of the Biochemistry Department, the synthesis and structural analysis of compounds containing flavin and nicotinamide moieties covalently linked by a propylene bridge. These compounds, in their various oxidation states, are model compounds designed to reveal the electronic interactions of flavin and nicotinamide rings. Their structures could shed light on the mechanism by which flavins reduce nicotinamide containing molecules. The synthesis of one of these model compounds has been completed. What remains is to crystallize it in its various oxidation states and to work out the X-ray structures of these crystals.

In the structural analysis of the yeast enzyme pyrophosphatase, we continue to make good progress. In the past year we have located two major substitution sites of HgI_4^{-2} in the crystal. We are now engaged in the process of collecting diffraction data.

Publications:

Bunick, G., McKenna, G. P., Colton, R. and Voet, D., "The X-Ray Structure of Yeast Inorganic Pyrophosphatase, Crystal Data", J. Biol. Chem. 249, 4647 (1974)

Bunick, G. and Voet, D., "Crystal and Molecular Structure of 9-β-D-Arabinofuranosyladenine", Acta Cryst. B30, 1651 (1974)

Shieh, H.-S. and Voet, D., "The X-Ray Structure of the Molecular Complex 9-Ethyladenine · Parabanic Acid · Oxaluric Acid Monohydrate", Acta Cryst. (Accepted)

Voet, D., "Intermolecular Interactions in Adenine · Barbiturate Complexes", in Molecular and Quantum Pharmacology, Eds., E. Bergman and B. Pullman, R. Reidel, Dordrecht-Holland, 1975, p. 429

B. SURFACES AND INTERFACES

1. Kinetics of Surface-Catalyzed Reactions

W. R. Brennen, Associate Professor of Chemistry

Research Assistants: R. V. Gutowski
M. E. Shuman

Support: NSF-MRL

Objective and Approach: The objectives of this work are (i) to investigate the factors which affect the rate at which atoms recombine to form molecules on various interesting and important surfaces; (ii) to try to characterize the sites at which recombination events occur; (iii) to investigate energy disposal in surface recombination; (iv) to explore modification of surface structure as a way of controlling catalytic activity; and (v) more broadly, to form a coherent molecular picture of surface catalyzed reaction events.

Our approach involves both experimental work and computer modelling. With the computer we are working out the macroscopic kinetic consequences of various likely molecular mechanisms of surface recombination combined with diffusive transport in order to establish a basis for comparison with experiment. Experimentally, we are developing a time-resolved version of an older steady-state method for studying the kinetics of nitrogen atom recombination on the surface of materials having a wide range of catalytic activity, such as silica in various forms, chemically modified silica, and transition metal films.

This work bears on the general problem of catalysis as well as on practical questions concerning materials performance in energetically and chemically hostile environments. Our long-range goal is to contribute to a better inderstanding of surface processes at the molecular level.

Progress: We have completed carrying out computer modelling of the Langmuir-Rideal mechanism of surface recombination. This mechanism views the recombination as occurring in two steps. An atom impinging on a catalytic surface has a certain probability of encountering an active site and being adsorbed. An adsorbed atom resides on the surface for an average time, τ, whereupon its residence may terminate by desorption or by abstraction by a second atom striking it from the gas phase and carrying it off immediately as a diatomic molecule. This particular mechanism discounts the possibilities that (i) adsorbed atoms may hop from site to site on the surface, (ii) that adsorbed atoms may be collisionally desorbed, and (iii) that newly formed diatomic molecules may reside for a significant time at the site where they are formed. The question of whether or not these

possibilities may be safely ignored must be viewed as open with respect to any particular choice of catalytic surface or reactant atom. We have computed families of solutions to the coupled differential equations governing the kinetics of the simple two-step mechanism described above for broad ranges of the characteristic parameters. These solutions have been compared with approximate descriptions of the kinetics based on various forms of the quasi-steady-state (Bodenstein) hypothesis in an effort to sharpen our appreciation for the circumstances in which the steady-state approach does or does not provide a fair description of the kinetics. As expected, the probability of a gas atom striking the surface being removed forever from the system depends in general on the time which has elapsed since the virgin surface was first exposed to impinging atoms, and continues to do so until the surface coverage has reached a stationary value. In the literature of this subject the above-mentioned probability, called γ, has always been assumed to be a <u>constant</u> characteristic of the surface.

In order to apply our model in realistic physical circumstances suitable for time-dependent experiments, we have chosen to reconsider the Smith side-tube method. In this method a cylindrical tube whose inner surface is the material of interest is exposed at one end to a reservoir containing a constant concentration of atoms. The atoms diffuse through the background gas into the side tube, interact with the walls, and eventually set up a stationary distribution of atomic concentration. Previous work has focused exclusively on the stationary distribution. We wish to observe how the distribution is built up in time. To model this kind of experiment requires solving the diffusion equation, incorporating the time-dependence of γ into the boundary conditions, and including the complicating effects of homogeneous recombination. The description of the surface mechanism is built into the boundary conditions, whereas the diffusion and homogeneous recombination merely govern the rate at which atoms strike a given patch of the wall at a given time. Up to now we have succeeded in carrying out this computation for constant γ and without including the homogeneous process. Inclusion of the homogeneous process, which is second-order in atom concentration, makes the partial differential equation non-linear, and we are currently engaged in learning to deal with this complication.

Publications:

Brennen, W., Gutowski, R. V. and Shane, E. C., "Vibrational Distributions of N_2 $(A^3\Sigma_u^+)$ in the Nitrogen Afterglow", Chem. Phys. Lett. <u>27</u>, 138 (1974)

Brennen, W. and Shuman, M. E., "A New Example of Formal Non-Steady-State Kinetics. A Model of Heterogeneous Atom Recombination", J. Phys. Chem. <u>79</u>, 741 (1975)

2. Electronic Structure and Interaction of Surface Atoms by Angular Correlation Experiments

M. E. Caspari, Professor of Physics

Research Assistant: D. J. Bellafiore

Support: ARPA-LRSM

Objective and Approach: Recent technical developments have made detailed and reliable investigations of clean surfaces possible. These experiments have yielded reproducible and informative results regarding the structure of surfaces as well as the distribution, energetics and electronic structure of surface atoms and atoms adsorbed on surfaces. Studies of surfaces have both fundamental as well as practical interest. Thus, catalysis and many biological processes involve surface phenomena. The structure of electrons surrounding surface atoms or atoms adsorbed on a clean surface is markedly different from that of electrons in the bulk. Furthermore, surface atoms interacting with each other represent a two-dimensional network with its own particular properties, which are of great importance to our understanding of the structure of matter. Direct information regarding the electronic structure of surface atoms can be obtained by nuclear techniques and, in particular, by the method of Perturbed Angular Correlations. This experiment involves a measurement of the perturbation of the radiation pattern of nuclear gamma rays, following the decay of radioactive surface atoms, by the electrons on the surface. The nucleus acts in this way as a direct probe of the electronic structure in its vicinity. Since Perturbed Angular Correlation experiments require only very few atoms, they are extremely suitable for such direct probe measurements of the electronic structure of surface atoms.

Progress: Originally, it was planned to use the 49 minute half-life isomeric state of Cd^{111m}. This isotope was successfully produced at the University of Pennsylvania Tandem Accelerator by the $Pd^{108}(\alpha, n)Cd^{111m}$ reaction. However, due to the recent acquisition of an improved accelerator by the Tandem, the possibility of using this facility has been delayed until renovations are completed. The new machine will provide us with higher energy α-particles and thus increase the production rate of radioactive Cd^{111m}. In the meantime, we have decided to use the radioisotope In^{111}.

In^{111} is a 65 hour half-life isotope which decays by electron capture to an excited state of Cd^{111}. The subsequent decay of this excited state to the ground state of Cd^{111} by the emission of two successive γ-rays exhibits a good angular correlation which can be used to study the effects of the environment. Since the nuclear cascade in Cd^{111m} ($11/2^-$ -146 kev $\gamma \rightarrow 5/2^+$ - 247 kev $\gamma \rightarrow 1/2^+$) and that produced by the decay of In^{111} ($7/2^+$ - 172 kev $\gamma \rightarrow 5/2^+$ - 247 kev $\gamma \rightarrow 1/2^+$) both involve the same intermediate state ($5/2^+$), we would expect that the observed behavior would essentially be isomorphic

provided the electron captured during the initial decay of In^{111} does not significantly affect the electronic configuration seen by the intermediate state.

The application of the technique of perturbed angular correlations can easily be extended to the problem of catalysis, and we are planning to do so. By depositing a monomolecular layer of radioactive material on a clean single crystal surface and observing the changes in the angular correlation pattern as a function of the adsorbed gas type and coverage, the character of the interactions between the surface and the gas can be determined. Since the technique is sufficiently general, any of a number of gases, such as H_2, CH_4, CO, CO_2, and O_2, can be employed.

In addition, the study of interfaces and the transition of surface properties to bulk properties can also be studied by depositing more material on the monomolecular layer of radioactive atoms and studying the changes in the angular correlation pattern as a function of thickness. Clearly, there should be a point at which the observed behavior resembles that of an atom in a solid. We plan to investigate this topic by evaporating additional amounts of cadmium and tungsten after a layer of radioactive atoms has been put on the surface.

3. Quantum-Mechanical and Statistical-Mechanical Studies

D. D. Fitts, Professor of Chemistry

Research Assistants: M. L. Law
W. G. Madden
. J. Welsh, Jr.

Support: NSF-MRL
U of P

Objective and Approach: From a knowledge of the interactions among molecules, it is possible in principle to predict the structure and the macroscopic properties of materials and the dynamics of processes. Thus, the objective of our overall research program is two-fold: to evaluate the potentials of interactions for various systems as quantitatively as possible and to study by means of statistical mechanics the influence of these potentials on the structure and properties of macroscopic systems. The results of such research provide a basic understanding of the properties of materials and of the dynamics of molecular processes.

The technological importance of adsorption in the fields of catalysis, of oxidation and corrosion of surfaces, and of isotope separation has led us to explore the fundamental molecular processes involved. To this end we are determining the forms of the intermolecular potential functions for adsorbate-surface and for adsorbate-adsorbate interactions. Our immediate aim is to provide a detailed understanding at the molecular level of the influence of surface sites on the adsorbate energy levels.

The application of statistical mechanics to determine structure and macroscopic properties from the known or assumed form of the intermolecular potential is often a difficult mathematical task. We are applying perturbation techniques to the distribution function procedures of the theory of fluids in order to calculate quantitatively the structure and thermodynamic properties of simple and polar fluids. Our goal is to develop a scheme for determining the structure and bulk properties for highly-structure liquids such as water.

Progress: During the year 1974-75 we worked on two distinct problems: adsorption on solid surfaces and perturbation theory of fluids.

Adsorption on Solid Surfaces

We are presently studying the fundamental problem of determining the intermolecular potential functions for adsorbate-surface interactions. We have just calculated the wave functions and energy levels for the system consisting of a diatomic molecule interacting with a uniform surface according

to an anisotropic potential form proposed by Neilson and Gordon. The initial form for the Schrödinger equation has five variables, but three of them are readily separated off leaving a coupled differential equation of two variables. We separated this differential equation by a decoupling method derived from the calculus of variations and obtained six decoupled equations (two differential equations and four integrals) in six unknowns. These six unknowns are two wave functions (one for each of the two variables) and four coupling or Lagrange-type parameters. These six equations must be solved simultaneously by an iterative procedure. We have developed the computer programs for obtaining the eigenfunctions and eigenvalues for each of the differential equations and have obtained the solutions for the three lowest energy states.

We are now in a position to calculate various expectation values and to compare the energy levels for the adsorbed diatomic molecules with the energy levels for the diatomic in the gas phase. In addition, by summing the potential form over lattice points on the solid surface, we can generalize our results to a nonuniform surface. These applications are currently under investigation.

Perturbation Theory of Fluids

In recent years a number of perturbation schemes for the radial distribution function (RDF) of a simple fluid have been developed. The basic procedure is to expand the RDF for a fluid whose molecules interact according to a particular pair potential about the RDF for a reference fluid. During the past year we have developed a new perturbation procedure for determining the RDF for a fluid whose molecules interact according to the Lennard-Jones potential by using the Percus-Yevick (PY) and hypernetted-chain (HNC) integral equations to approximate the perturbation corrections. In both cases the infinite perturbation series can be summed in closed form. The contribution of the attractive part of the pair potential to the RDF is treated as a perturbation to a reference system whose molecules interact according to the repulsive part of the potential. The RDF of the reference system is expanded about the RDF for a fluid of hard spheres of diameter d. We proposed and tested five criteria for the determination of d. Excellent agreement between the calculated RDF and computer simulations are obtained over a wide range of densities from the HNC perturbation treatment for the attractive intermolecular forces and the PY perturbation expansion for the repulsive forces with the hard-sphere diameter d given by a PY compressibility criterion which we have proposed. In terms of numerical accuracy this perturbation scheme is the best one that has been developed. This work has been accepted for publication by Molecular Physics.

Our attempts to develop a perturbation scheme for the RDF of polar fluids have also been successful. In collaboration with Dr. W. R. Smith at Dalhousie University (Halifax, Nova Scotia) we have determined via perturbation theory the RDF for a fluid whose molecules interact as hard spheres

plus a dipole-dipole dispersion term. In this case the molecules of the reference fluid interact according to a spherically-symmetric reference intermolecular potential in which a contribution from the anisotropic dipole-dipole term is included. The perturbation scheme is devised so that the first-order perturbation correction vanishes. We find that the RDF for the resulting reference system agrees remarkably well with computer simulations for the fluid with the full dipolar hard-sphere potential. This is the first successful theoretical calculation of the RDF for this system.

We have also applied perturbation theory to determine the RDF for fluids whose molecules interact via a Lennard-Jones potential plus a dipole-dipole term (Stockmayer potential) and via a Lennard-Jones potential plus a quadrupole-quadrupole term. For these fluids we have selected the Lennard-Jones fluid as the reference system and have calculated the first-order perturbation correction in each case by the HNC procedure mentioned above. The agreement with computer simulations using the complete potentials is excellent. We have also calculated the second-order perturbation correction in each case and found that the agreement with computer simulations worsens, although it is still fairly good. This situation indicates that the perturbation expansion is not rapidly convergent. We are currently seeking other reference systems which will give smaller perturbations.

Publications:

Law, M. L. and Fitts, D. D., "Comparison of Argon-Argon Interatomic Potentials from Elastic Molecular-Beam Scattering Data", Mol. Phys. 29, 1933 (1975)

Madden, W. G. and Fitts, D. D., "Integral-Equation Perturbation Theory for the Radial Distribution Function of Simple Fluids", Mol. Phys. (Accepted)

Madden, W. G. and Fitts, D. D., "A New Perturbation Technique for the Radial Distribution Function of Simple Fluids", Mol. Phys. 28, 1095 (1974)

Madden, W. G. and Fitts, D. D., "On the Calculation of a Corrected Radial Distribution Function", J. Chem. Phys. 61, 4935 (1974)

Madden, W. G. and Fitts, D. D., "Perturbation Theory for the Radial Distribution Function for Simple Polar Fluids", Chem. Phys. Lett. 28, 427 (1974)

Madden, W. G. and Fitts, D. D., "A Re-examination of the HNC Theory for the Radial Distribution Function", J. Chem. Phys. 61, 5475 (1974)

4. High Resolution Microscopy of Crystal Interfaces

W. R. Graham, Associate Professor of Metallurgy and Materials Science

Research Assistant: P. G. Flahive

Support: NSF-MRL

Objective and Approach: Progress in our efforts to understand surface-adsorbate bonding and surface reaction mechanisms is critically dependent on our ability to characterize interactions at the atomic level and to directly determine the geometric location of active adsorption sites. To this end, we have initiated a research program which will utilize the unique capabilities of the field-ion microscope (F. I. M.). The characterization of surface interactions by F. I. M. studies of surface diffusion is well established, and the precise determination of the binding sites of self adsorbed tungsten atoms has recently been demonstrated.

Commercially available field-ion units fall far short of our stringent requirements in ultra-high vacuum, image intensification and many other technical areas. We have thus undertaken the construction of two field-ion microscopes of our own design. Progress on the first system should allow trial operation within the near future.

Our research program will involve studies of both metal and semiconductor surfaces.

a) Metal Surfaces. An initial study of the accommodation process for self adsorbed tungsten atoms will precede work with nickel surfaces. Study of nickel surfaces will allow a close coordination of our program with that of the surface theorists.

b) Semiconductor. Our immediate aim will be the development of a reliable imaging technique for semiconductor surfaces - a necessary prerequisite to subsequent surface diffusion studies.

Progress: The construction of two field-ion microscopes was initiated at the outset of this program in September of 1974. The first of these systems is progressing quite reasonably well with the completion of the pumping station and gas handling system. Preliminary testing of this system showed that a vacuum of 10^{-10} torr was attainable after a single bake at 320°C. The microscope tube is nearing completion and full testing of the system will commence in the near future.

Publications:

Graham, W. R. and Ehrlich, G., "Direct Identification of Atomic Binding Sites on a Crystal Surface", Sur. Sci. 45, 530 (1974)

Graham, W. R. and Ehrlich, G., "Direct Measurement of the Pair Distribution Function for Adatoms on a Surface", Phys. Rev. Lett. 32, 1309 (1974)

Graham, W. R. and Ehrlich, G., "Surface Diffusion of Atom Clusters", Brit. J. Phys. F 4, 212 (1974)

Graham, W. R. and Ehrlich, G., "Surface Self Diffusion of Single Atoms", Thin Solid Films 25, 85 (1975)

5. Reaction Kinetics and Mechanisms

J. G. Miller, Professor of Chemistry

Research Assistants: J. J. Davis
G. A. Parodi
B. Vessal

Support: NSF-MRL

Objective and Approach: The scientific objective of our work is to determine in more complete detail the mechanism of two chain reactions. The first of these is the reaction of haloalkanes with amines and the second is the decomposition of peroxyesters.

Chain reactions such as those we are studying do not take place until an initiator is brought into the system of reactants. The initiators are of a wide variety and include light radiation, thermal energy, active surfaces, and certain molecules and ions.

We have accomplished detailed self-consistent information on the initiating, propagating, and terminating steps of the haloalkane-amine reaction for two types of initiators and are now concentrating on the molecular-structural details of the initiation by metal surfaces and by metal ions.

At present, the peroxyester decomposition is being studied only with light radiation as initiator. Both chemical-kinetic and spectroscopic methods are being used to determine the mechanism of that chain reaction in its several steps.

Progress: The photochemical reaction of the amines with haloalkanes has been studied by us in all of its stages. Mechanisms for the initiation, propagation, and termination have been constructed in good detail and over-all consistency. Our latest work on that reaction (J. Amer. Chem. Soc. 96, 3813 (1974)) focused on the initiation process and showed clearly that an electron donor-acceptor complex forms between the amine and haloalkane and is changed to an exciplex on irradiation. The exciplex decomposes spontaneously to form an intimate ion-pair and one of the carriers. The ion-pair then reacts with amine to form the other carrier.

Our other principal interest in that chain reaction has centered on the initiation at a metallic copper surface activated by oxygen. This initiation was discovered by our group and we have published (J. Amer. Chem. Soc. 92, 2946 (1970)) a kinetic study of it that showed that here, too, an electron donor-acceptor complex plays an important role. The complex forms after the amine is first adsorbed on active sites formed by the oxygen with the copper. When the haloalkane forms the complex with the adsorbed amine,

the oxygen at the site causes the completion of the charge transfer, forming the carrier and producing a copper(I) salt.

The role of the oxygen in the completion of the charge transfer and the rapid dissolution of the metal is now being investigated by our group. Despite its complexity, it has considerable appeal because of its importance to the understanding and prevention of the corrosion of metals by small amounts of oxygen.

We are trying to simplify the study by using sulfur in place of the oxygen, principally to permit better control of the concentration of oxidant and to avoid the side-reactions caused by oxygen. Progress in this effort is slow due to the great difficulty of excluding oxygen entirely.

We are also starting study of several of the initiation steps by means of reflectance spectroscopy. The adsorption of the oxygen and of the amine should be amenable to such study and we hope that the other two steps can also be studied in that way. The initiation by copper ions in the homogeneous liquid phase is also being investigated.

In the photolysis of the t-butoxy esters of long-chain aliphatic peroxyacids we have found that small amounts of pyridine have a remarkably great effect. Pyridine is used in the synthesis of these peroxides and is extremely difficult to remove completely, so that its effect of lowering the quantum yield has not been noticed before. The pure peroxyesters show a much higher quantum yield due to chain reaction. We are studying the radical carriers of that reaction by use of EPR spectroscopy.

Publication:

Kiselev, V. D. and Miller, J. G., "Experimental Proof that the Diels-Alder Reaction of Tetracyanoethylene with 9, 10-Dimethylanthracene Passes through Formation of a Complex between the Reactants", J. Am. Chem. Soc. 97. 4036 (1975)

6. Statistical Mechanics of Adsorption in Micropores

A. L. Myers, Professor of Chemical and Biochemical Engineering

Research Assistant: E. Glandt
C. Minka

Support: NSF-MRL
NSF
MOC
U of P

Objective and Approach: Adsorption on flat surfaces has been studied exhaustively but there are no practical equations for adsorption in microporous adsorbents. This is surprising in view of the industrial importance of zeolites for separations and catalysis.

Adsorption in micropores is given theoretically by the equation:

$$\overline{N} = \frac{\Sigma i Z_1 (P/kT)^i / i!}{1 + \Sigma Z_1 (P/kT)^i / i!}$$

where the summation terminates at M, the capacity of a cavity (10-20 molecules). Z_N is the configuration integral for N molecules in a cavity and even Z_1 is a complex summation over hundreds of atoms in the lattice followed by integration over the cavity. So far, attempts to calculate configuration integrals from first principles have been unsuccessful because of the lack of a quantitative theory of intermolecular forces. Therefore our approach is to use experimental data for the first configuration integral (Z_1) as a probe of adsorbate-surface intermolecular forces. Given intermolecular potentials for adsorbate interactions with lattice atoms, one can calculate the higher configuration integrals and thus generate all of the equilibrium properties of adsorption at different temperatures from low pressure up to saturation.

Monatomic gases (Ar, Kr, Xe) are ideal molecular probes because complexities of polarity and hindered rotation are removed. Also, need for removal of krypton and xenon formed during fission of nuclear fuels provides a practical motivation for these studies.

Progress: Research over the past two years has yielded several accomplishments in 1974-75. We are publishing a series of papers on this work, the most important results of which are summarized as follows:

We chose to study adsorption in zeolites (MS-5A, MS-13X) because the cavities are all the same size (cf. carbons and silica gels which have a wide distribution of pore sizes). The surface of the zeolite cavity is composed mainly of oxygen atoms and a smaller number of ions (Na, Ca). For

adsorption of nonpolar molecules (Ar, Kr, Xe, CH_4, etc.) the most important adsorbate-surface interactions are dispersion forces.

At low coverage the problem is to calculate the configurational integral for one molecule in a cavity. In the integrand, one must sum the interactions of this molecule over about 100 surface atoms. Although coordinates for the surface atoms have been derived from crystallographic data, a direct summation is time-consuming. We developed a model similar to the Lennard-Jones and Devonshire model for liquids in which atoms in the surface are distributed uniformly on the surface of a sphere whose radius is equal to the average distance of the surface atoms from the center of the cavity. This LJD model agrees quite well with a direct lattice summation.

For calculations of the first configurational integral, the only unknown is the pair potential for the adsorbate molecule and a surface oxygen atom. We determined the value for Ar-O from experiment, from which values for other adsorbates can be calculated from the law of corresponding states. Using one constant for the well depth of the Ar-O potential, we were able to calculate first configurational integrals as a function of temperature for a series of nonpolar molecules adsorbed in different zeolite cavities. Agreement with experiment is excellent.

At higher coverage the problem is to calculate higher order configurational integrals for 1, 2, 3··· molecules adsorbed in a cavity. A series of Monte Carlo experiments were performed on a computer to test various theories such as hard-sphere adsorbate molecules and the LJD smeared model for surface atoms. The most important finding was that the LJD model, although adequate for the first configurational integral, fails for higher integrals because the heterogeneous surface, by the action of high energy sites, weakens cooperative forces between adsorbate molecules.

The conclusion is that surface heterogeneity cannot be neglected if potential parameters are to have physical meaning. It is interesting that the same conclusion has been reached for adsorption on plane surfaces, and perhaps should have been anticipated. The success of the homogeneous LJD model for the first configurational integral is fortuitous and does not extend to higher integrals.

Publications:

Myers, A. L., Bonacci, J. C. and Eagleton, L. C., "The Evaporation and Condensation Coefficient of Water, Ice and Carbon Tetrachloride", Chem. Eng. Sci. (Accepted)

Myers, A. L. and Glandt, E., "Thermochemical Production of Hydrogen by Decomposition of Water", Ind. Eng. Chem., Process R & D (Accepted)

Myers, A. L. and Seider, W. D., Introduction to Chemical Engineering and Computer Calculations, Prentice-Hall (1975) (Accepted)

7. Electron Spectroscopy of Surfaces

E. W. Plumm. r. Associate Professor of Physics

Postdoctoral Fellow: T. Gustafsson

Research Assistants: S. P. Weeks
S. L. Weng

Support: NSF-MRL
NBS
ARPA-LRSM
NSF

Objective and Approach: The objective of this program is to determine the fundamental properties of the chemical bond at a surface. The premise of this program is that such a fundamental understanding of chemisorption would surely accelerate the development of a mechanistic understanding of such practical materials orientated problems as Heterogeneous Catalysis, Corrosion, Embrittlement, Photocells and many Solid-State Electronic Devices. The achievement of such an objective necessitates a close coupling between theory and experiment, focusing, at first on a few carefully chosen systems. We will concentrate on the adsorption and interaction of simple diatomic molecules such as H_2, CO, O_2, and N_2 on well-defined metal substrates of the late transition elements, such as Ni, Fe, Co, Pd, etc.

The experimental approach will use electron emission spectroscopies to determine for a static system: (1) the atomic species present on the surface (Auger); (2) the two dimensional ordering (LEED); (3) the electronic energy level spectrum (Photoemission and Field Emission); and (4) the geometrical arrangement of the adsorbates as well as each orbital (Angular-Energy resolved Photoemission). Mass spectrometry combined with photoemission will be used to investigate dynamic effects, using beamed gas sources. This information coupled with theoretical calculations of electronic energy levels, bond energy and configuration will be used to determine How and Why a given bonding configuration results when gas A is adsorbed on a surface of metal B.

Progress:

Program Status: Present

1. All of the special components for the ultra-high vacuum, "Do Everything", surface system have been designed, and are built or being finished at this time. This includes: (1) A specially designed windowless UV light source with better than nine orders of magnitude pressure differential, while maximizing the light output; (a) A modification of a Faraday

cup, retarding type of energy analyzer, to accommodate an electron multiplier and sample only ± 2.0 in angle over any azimuthal or polar angle; (3) the design of a UHV compatible, cryogenic specimen manipulator with three degrees of freedom for motion of the sample over a temperature range of 30 K to 3000 K; and (4) A high pressure gas cell to do gas phase photoionization cross section measurements.

2. We have utilized the NSF sponsored 240 meV storage ring at the Physical Sciences Laboratory of the University of Wisconsin to study the photon dependence of the photoemission spectra of chemisorbed atoms and molecules.

This has been a very successful joint program with Dr. D. Eastman of IBM (see Major Accomplishments), and will be expanded in the future (see Future Directions).

Major Accomplishments:

1. The first (non-trivial) identification of chemisorbed energy levels was made for CO adsorbed on Ni and Pd by measuring the photoionization cross section of the valence orbitals as a function of photon energy. These measurements when compared to our measurements for gas phase CO indicated quite unambiguously the proper identification of the chemisorbed energy levels. This measurement has had a considerable impact on quantitative comparison of theory and experiment (see Schrieffer and Soven). They also have shown that the photon dependence of the photoionization cross section is a fingerprint of the orbital (see Schrieffer and Soven).

2. The photon dependent measurements outlined above have shown quite conclusively that the surface sensitivity of photoemission to a given adsorbate level is dictated primarily by the energy dependence of the photoionization cross section, not by the mean free path of the escaping electron. The surface sensitivity is not nearly as simple as one had believed.

3. The higher photon energies available at the Storage Ring allowed us to observe the near-core levels of oxygen (2S) and carbon monoxide (3σ) during adsorption on tungsten. Since the 3σ level of CO is intimately involved in the bonding of CO it is imperative to observe this level when addressing the question of dissociation of CO. We have shown that the high temperature-ordered state of adsorbed CO is in fact dissociated as our UV work indicated, but that the lower temperature states still have some residual bond between the carbon and oxygen. Our UV data showed that both the carbon and the oxygen atom were bound to the substrate in both of these states.

Future Program Direction:

1. Our work with gas phase CO has shown us how important it is to understand the simple molecule. We will begin a modest program in gas

phase photoelectron spectroscopy of simple molecules which are relevant to our chemisorption case, for example CO, $Ni(CO)_4$, to bridge bonded carbonyls, etc. These measurements will include photon dependence of the cross section of each energy level as well as the photon dependence of the angular dependence. The major objective will be to check theoretical calculations of the angular dependence of these molecules (see Schrieffer and Soven) in the gas phase. These measurements and theoretical calculations will give us the fundamental information needed to understand the angular-energy resolved emission from a surface molecule.

2. The sulfur on Ni systems will be investigated immediately with angular resolved photoemission and Auger to determine the geometrical position of the sulfur atom. These results will be compared with existing LEED data as a check on both techniques.

Publications:

Gustafsson, T., Plummer, E. W., Eastman, D. and Freeouf, J., "Interpretation of the Photoelectron Spectra of Molecularly Adsorbed CO", Solid State Comm. 17, 391 (1975)

Leibson and Plummer, E. W., "Theory of Angular Dependence of Photoemission UHE Shapes from Adsorbates", J. Chem. Soc. Faraday II (1975) (Accepted)

Plummer, E. W., "The Applicability of Electron Emission Spectroscopies to Elucidate Chemisorption", Physical Basis for Heterogeneous Catalysis, Gstaad Swit., Sept. 1974, Published in Battelle Colloquium

Plummer, E. W., "Experimental Observations of Electronic Energy Levels at a Solid-Vacuum Interface", J. Electrochem. Soc. 121, 1186 (1974)

Plummer, E. W., "Field Emission Work Function", Sur. Sci. 48, 417 (1975)

Plummer, E. W., "Photoemission and Field Emission Electron Spectroscopies", Topics in Applied Physics, Ed., R. Comer, Springer-Verlag

Plummer, E. W., Gadzuk, J. W. and Penn, D. R., "Vacuum-Tunneling Spectroscopy", Phys. Today 28, 63 (1975)

Plummer, E. W., Waclawski, B. J. and Vorburger, T., "Photoelectron Spectra of the Decomposition of Ethylene on (110)W", Chem. Phys. Lett. 28, 510 (1974)

8. Theory of Chemisorption and Catalysis

J. R. Schrieffer, Mary Amanda Wood Professor of Physics

Postdoctoral Fellows: J. B. Danese
A. Liebsch

Research Assistants: J. W. Davenport
G. Loubriel

Support: NSF-MRL
NSF
ARPA-LRSM
ARPA

Objective and Approach: Our primary objective is to develop a quantum theoretic understanding of the electronic and conformational structure of chemisorption systems in which atoms and/or small molecules interact with metal surfaces. We are investigating the one electron excitation spectra, as observed in photoemission and field emission spectroscopies, as well as the potential energy functions for simple surface reactions and such as adsorption and dissociation. Ultimately we plan to extend our analysis to more complex reactions such as the methanation of carbon monoxide, hydrogen-deuterium exchange, etc. This work is of fundamental importance in gaining a microscopic understanding of heterogeneous and homogeneous catalysis, with the development of a high activity, high selectivity, rugged CO methanation catalyst being one of the most important goals in coal gassification technology. The catalytic formation of water from H_2 and O_2 is of great importance in fuel cells. At present, essentially no microscopic understanding of these extremely important reactions exists, yet variation of activity by 5 to 10 orders of magnitude occur for modest changes of surface composition. We are developing extensions of the self-consistent multiple scattering (or Green's function) technique which accurately includes the so-called "non-muffin tin" corrections often neglected in this scheme, but which play an exceedingly important role, in determining the potential energy functions for surface reactions as well as one-electron spectroscopies. In a separate research program we are studying a domain wall excitation in displacive lattice transitions which is related to ferroelectrics and Peierls distortion systems.

Progress: During the past year our theoretical program in surface physics has had two major thrusts. The first (a) is the development of self-consistent multiple scattering analyses of photoemission processes for simple adsorbates on clean metal surfaces and for polyatomic clusters. The second (b) is the development of efficient methods for improving the conventional muffin-tin potential multiple scattering technique for determining one-electron spectra and potential energy functions for polyatomic complexes. Based on our

earlier LCAO-MO analysis, it appears that the chemisorption bond can be treated in zero order as localized to the first and second coordination shell of atoms surrounding the adsorption site. Thus a surface complex is a plausible starting point. We are studying ways to incorporate this complex into the remaining indented solid to form a complete picture, thereby making a graded approximation scheme with most emphasis being placed on the bonding region. Also we are beginning an investigation of dynamic relaxation effects which are of importance in unravelling the physical origin of valence level shifts resulting from chemisorption bonds as observed by photoemission.

(a) Based on work begun last year ('73-'74), Ansgar Liebsch has continued to investigate the effects of multiple scattering of the outgoing electron in photoemission from solid surfaces. Using the layer KKR multiple scatterings scheme familiar in low TaS_2. Qualitative agreement with experiment is obtained if he uses a localized atomic (Ta-d) orbital for the initial state, however band structure effects appear to be essential if detailed agreement with experiment is to be obtained. Liebsch is also applying the layer KKR scheme to treat photoemission from a periodic overlayer on a clean metal surface. Finally, Liebsch has been working with P. Soven and N. Kar on the theory field emission spectra from clean surfaces.

James W. Davenport has made a major step forward in developing a multiple scattering scheme which treats on a common basis both initial and final state effects using a self-consistent muffin-tin potential for a polyatomic cluster. The computer program is now working and he is using this scheme to determine both the energy dependence of the total photoemission cross section (an extremely important tool in experimentally unravelling observed valence levels) and the angular photoelectron distribution. Furthermore significant changes of emission rates occur for different polarizations of light. This work is being closely correlated with the experimental program of Plummer and Gustafsson and appears to have great promise in making detailed interpretation of photoemission distributions possible.

(b) J. Bryan Danese has developed efficient numerical methods for taking into account non-muffin-tin effects in the one-electron spectra and in the potential energy functions for polyatomic clusters. The standard muffin-tin approximation for the self-consistent potential, while giving a reasonable first approximation for one-electron excitation energies, leads to qualitatively incorrect results for binding energy curves in most cases, e.g., the C_2 molecule is unbound for all interatomic spacings. Treating the non-muffin-tin potential in perturbation theory gives remarkably good bond energies and equilibrium spacings for a series of diatomic molecules. Danese has now programmed these perturbation corrections for both the one-electron spectra and binding curves for general clusters of up to seven atoms, with extension to larger clusters being simply achieved by redimensioning the relevant memory blocks. It appears that this technique will provide a sufficiently accurate and simple method so that one can study potential energy functions

for chemisorption, dissociation, etc. to gain an understanding of activation energies and binding energies of various surface complexes. Calculations are proceeding on the Ni_xCO system.

Finally, a theoretical analysis of a one-dimensional chain model of anharmonic lattice dynamics has been carried out in collaboration with Prof. J. A. Krumhansl of Cornell University. The concept of domain walls in the low temperature distorted phase of the model was established by showing that these excitations, along with the phonon excitations, could reproduce the exact low temperature form of the free energy as well as the equal time lattice displacement correlation function. When the domain wall excitations are included in a calculation of the dynamic structure factor, a central peak is obtained whose width varies exponentially with universe temperature. Recent molecular dynamics calculations by T. R. Koehler of IBM-San José on a chain of 1000 mass points clearly show the existence and dynamical significance of domain walls. This work has been extended to two dimension by treating an array of parallel interacting chains. A sharp phase transition is obtained, in which one-dimensional quasi-long range order goes over to true two dimensional order. This work is relevant to the TCNQ program of Professors Heeger and Garito.

Publications:

Davenport, J. W., Einstein, T. L., Soven, P. and Schrieffer, J. R., "Theory of Chemisorption in Relation to Heterogeneous Catalysis", Proc. of the Battelle Colloquium on Physical Basis for Heterogeneous Catalysis, Gstaad, Switzerland, Sept. 1974, Plenum Press, N. Y. (in press)

Einstein, T. L., "Changes in Density of States Caused by Chemisorption, with Implications for Photoemission", Sur. Sci. 45, 713 (1974)

Einstein, T. L., "Short-Chain Model of Chemisorption: Exact and Approximate Results", Phys. Rev. B 11, 577 (1975)

Krumhansl, J. A. and Schrieffer, J. R., "Dynamics and Statistical Mechanics of a One-Dimensional Model Hamiltonian for Structural Phase Transitions", Phys. Rev. B 11, 3535 (1975)

Liebsch, A., "Theory of Angular Resolved Photoemission from Adsorbates", Phys. Rev. Lett. 32, 1203 (1974)

Liebsch, A. and Plummer, E. W., "Theory of the Angular Dependence of the Photoemission Line Shape from an Adsorbate, Faraday Disc. Chem. Soc. No. 58 (1975)

Paulson, R. H. and Schrieffer, J. R., "Induced Covalent Bond Theory of Chemisorption", Sur. Sci. 48, 329 (1975)

Schrieffer, J. R., "A New Schema for Entropy", Proc. of the Amer. Philosophical Soc. 118, 538 (1975)

Schrieffer, J. R. and Soven, P., "Electronic Structure of Surfaces", Physics Today (Accepted)

Schrieffer, J. R. and Soven, P., "Surface Physics; Theory of the Electron Structure", Phys. Today 28, 24 (1975)

9. Electronic Structure of Surfaces

P. Soven, Associate Professor of Physics

Research Assistant: N. Kar

Support: NSF-MRL
ARPA-LRSM
NSF
U of P

Objective and Approach: The proposed research deals with the electronic structure of metal surfaces. The primary thrusts deal with calculation of electronic spectra and wave functions and with the prediction and explication of field emission experiments.

The surface of a metal is frequently the region of space where the interesting catalytic chemical reaction takes place. While the precise role of the metal substrate is uncertain (indeed, to ascertain this role is one of the underlying ultimate goals of the researcher) it is perfectly clear that a minimum role is to bind the reactants so that they do in fact react. Progress in understanding molecular binding has obviously been based on a knowledge of the electronic spectra of the component atomic species. Our work in the clean surfaces may be described as developing the same level of knowledge of one of the species in the chemisorption process (the substrate) that we already possess for the atomic adsorbate.

Progress: We have successfully programmed and tested our previously developed formalism for calculating the electronic energy level structure of thin films. We applied our method to copper films (monatomic and three layer) with satisfactory results. In view of the fact that other investigators have attempted to perform these calculations (obtaining, we believe, completely incorrect results) we find the successful calculations of the band structure of these films to be a significant accomplishment. It is one of our ultimate aims to carry these calculations through to self-consistency (in which case the electronic potential used to calculate the bands is in fact the one generated by the calculated wave functions) although it appears that our guess at the potential was in fact quite good. It is interesting that the result of the film calculations can be interpreted in a LCAO (linear combination of atomic orbitals) framework using nearly the same parameters as those applicable to the case of bulk copper.

We have completed the adaption of our programs necessary for the prediction of field spectra. Field emission is one of the few surface sensitive spectroscopies for which the underlying theory appears to be relatively well understood. The major obstacle to a detailed comparison of theory with experiment is not conceptual but rather resides in the complexity of the

materials studied. Successful completion of the programming will allow us to verify this view, with the ultimate aim being the use of field emission as a probe of surface electronic and (with some good luck) geometric structure.

Publications:

Schrieffer, J. R. and Soven, P., "Electronic Structure of Surfaces", Physics Today (Accepted)

Kar, N. and Soven, P., "Band Structure of Thin Films", Phys. Rev. B 11, 3761 (1975)

10. Electronic, Magnetic and Catalytic Effects Associated with the Interaction of Donor and Acceptor Molecules with Metallo Species

B. B. Wayland, Associate Professor of Chemistry

Research Assistants: L. F. Mehne
J. V. Minkiewicz
J. Swartz

Support: NSF-MRL
ARPA-LRSM
NIH

Objective and Approach: This study is focused on determining the influential factors for the binding of small molecules (O_2, NO, CO, N_2, SO_2) by metallo species and the mechanisms operative in modifying the electronic, magnetic and chemical reactivity properties through charge transfer interactions. Chemisorption, physisorption and the associated catalytic behavior of materials frequently result from donor-acceptor reactions. Interactions of this type may also be implicated in the introduction or modification of electrical conductivity and magnetic properties in materials. Interaction of small molecules with active binding sites of metallo species such as planar metal chelates, layered M-M bonded complexes and metals are studied, using spectroscopic and thermochemical methods. Variation of the metallo species and adsorbate molecules provides a systematic chemical approach for identifying essential features for the interaction. Modified chemical behavior and catalytic reactivity of chemisorbed species is examined and correlated with models for the coordination effects on structure and electron distribution.

Progress: A general bonding model describing the interaction of diatomic molecules with planar metallo sites has been developed and applied in anticipating the occurrence and principal structural and electronic properties of new materials of this type. Effects associated with varying the diatomic molecule were experimentally examined for series of species such as the 1:1 complexes of Co^{II} (porphyrins) with CO, NO and O_2. The relative position of the diatomic π^* levels with respect to the metal valence orbitals is found to play a significant and perhaps dominant role in the stability of these species. We have recently observed a variety of diatomic molecular complexes with d^3 to d^7 metal sites (d^3, Cr^{III}; d^4, Mn^{III}, Cr^{II}; d^5, Fe^{III}, Mn^{II}; d^6, Fe^{II}, Co^{III}; d^7, $Co^{II}(Fe^{I})$). Systematic studies of these materials have permitted experimental recognition of features dependent on the metal site electronic structure. For example, nitric oxide reacts with Cobalt(II) species to produce $Co^{III}(NO^-)$, but it interacts with manganese(II), resulting in $Mn^{I}(NO^+)$. The choice of metal center for chemisorption thus has a profound effect on the nature of adsorbed nitric oxide. The dramatic coordination induced electronic rearrangement in these complexes completely alters the diatomic molecule chemical reactivity. Modified chemical reactivity coupled with

facile reversibility make these materials useful in developing catalytic systems. We have observed reactions of oxygen and nitric oxide catalysed by iron(II) and cobalt(II) macrocycles. One example is the catalytic reactions of alcohols with nitric oxide in the presence of an Fe^{II} macrocycle to form alkylnitrites and hydrogen.

$$ROH + NO \xrightarrow{Fe^{II}(TPP)} RONO + \frac{1}{2} H_2$$

The search is continuing for metallo species that catalyze small molecule reactions such as $2NO + CO \rightarrow CO_2 + N_2O$; $2NO + 2CO \rightarrow N_2 + CO_2$; $CO + 3H_2 \rightarrow CH_4 + H_2O$. We have evidence for the reaction of coordinated NO reacting with a second NO to form coordinated N_2O_2, which is an important precursor in reducing nitrogen oxides.

Publications:

Mehne, L. F. and Wayland, B. B., "Properties of Ni(diphenylglyoximota)$_2$X (X = Br, I) in the Presence of Donor Molecules and in the Solid", Inorg. Chem. (Accepted)

Wayland, B. B. and Abd-Elmageed, M. E., "Phosphorus-31 Hyperfine Coupling in Tetraphenylporphyrin Cobalt(II) Complexes of Trivalent Phosphorus Ligands and Dioxygen Complexes: Substituent Effects on the Phosphorus σ Donor Orbital", J. C. S. Chem. Comm. 61 (1974)

Wayland, B. B. and Abd-Elmageed, M. E., "Tetraphenylporphincobalt(II) Complexes as a Probe for the Nature of Phosphine σ Donor Orbitals: Epr Studies of Phosphine and Dioxygen Complexes", J. Amer. Chem. Soc. 4809 (1974)

Wayland, B. B. and Kapur, V. K., "Epr and Electronic Spectral Evidence for Isomers Resulting from Basal and Axial Ligation of Bis(hexafluoroacetylacetonate)copper(II) by Triphenylphosphine", Inorg. Chem. 13, 2517 (1974)

Wayland, B. B. and Mehne, L. F., "A Comparison of AgMnO with Permanganate and Manganate Salts", Inorg. Nucl. Chem. (1974) (Accepted)

Wayland, B. B., Minkiewicz, J. V. and Abd-Elmageed, M. E., "Spectroscopic Studies for Tetraphenylporphyrin Cobalt(II) Complexes of CO, NO, O_2, RNC and $(RO)_3P$, and a Bonding Model for Complexes of CO, NO, and O_2 with Cobalt(II) and Iron(II) Porphyrins", J. Amer. Chem. Soc. 2795 (1974)

Wayland, B. B. and Olson, L. W., "Low Spin Nitric Oxide Complexes of Manganese Tetraphenylporphyrin", Inorg. Chemica Acta (Accepted)

Wayland, B. B. and Olson, L. W., "Spectroscopic Studies and Bonding Model for Nitric Oxide Complexes of Iron Porphyrins", J. Amer. Chem. Soc. 6037 (1974)

C. MATERIALS FAILURE CRITERIA

1. Deformation of Polymers

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Postdoctoral Fellow: Y. Imai

Support: NSF-MRL
ARO

Objective and Approach: The major mechanisms of polymer deformation are by shear and crazing. The primary objective is to determine how gases such as N_2, Ar, CO_2, and O_2 cause crazing which profoundly affects the strength of polymers. The crazes grow in the form of sponge-like, thin lenticular plates. Once the fundamental mechanism for the phenomenon is understood, then the criteria for the failure of particular polymer can be established in terms of the type of gaseous environment and the temperature and pressure of the gas. The basic approach is to study the effect of these gases on the nucleation and growth velocity of the individual crazes because the density and growth of the crazes are directly related to the macroscopic strength of the polymer.

The equilibrium and the dynamic properties of individual crazes will be observed. Equilibrium studies of crazes involve balancing the forces which cause a craze to either grow or recede. The dynamic studies involve measurements of the changes in velocity of crazes when either, the stress, temperatures or partial pressure of the gas is varied. These measurements not only provide an understanding of the microdynamics of a craze, but also provide measure of the diffusion of gases into polymers at very low temperatures.

Progress:

A. For the first time the yield point of a polymer has been measured as a function of the partial pressure of a gaseous environment: This has been done for several polymers in N_2 and Ar environments. It was found that for a constant partial pressure, the yield point <u>increases</u> as the temperature <u>increases</u> starting at 78 K. There is a critical temperature above which the yield point begins to decrease with increasing temperature. This is a very unusual effect because generally the yield point of polymers is known to <u>continuously decrease</u> with increasing temperature. The critical temperature varies with the polymer-gas combination that was used, and with the partial pressure of the gas as given in the table:

Polymer	Gas	Partial Pressure Atom	Critical Temperature °K where y.p. is a maximum
Polycarbonate	N_2	$\frac{1}{4}$	97
Polycarbonate	N_2	1	110
Polycarbonate	Ar	1	105
Kel-F	N_2	1	130
Kel-F	Ar	1	130

For each polymer-gas system there was found another temperature above which crazing ceased to be observed. At one atmosphere the critical temperature above which crazing is not observed is given in the following table:

	N_2	Ar	O_2(°K)
PC	123	122	125
PCTFE	180	180	180
PMMA	140	140	170

The change in Y. Pt. with pressure for several temperatures has provided a measure of the bonding energy of gas molecule to the surface of the polymer, e.g., the bonding energy of Ar to polycarbonate is about 1.3 kcal/mole.

B. For the first time the stress-strain curve of a polymer has been calculated in terms of the properties of the individual crazes. The properties which had been measured were the dependence of the craze density and velocity on stress, and the morphology of the individual crazes. The computer-calculated stress-strain curves were surprisingly similar to the experimental curves. Now it is possible to conceive the macroscopic stress-strain behavior of a polymer in terms of the microdynamics of the individual crazes. This result is comparable to the theory of dynamic yielding in crystalline solids in terms of the microdynamics of dislocations.

C. The polymers have been deformed at 78 K in N_2 at the widest possible speeds in both tension and compression. It was found (1) that the ln $\dot{\epsilon}$ vs y.p. is generally non-linear, (2) there is a critical speed in tension above which crazing is not observed and (3) N_2 has no effect for compressive loading. In polycarbonate crazing is not observed in Liquid/N_2 at strain rates above 200 min^{-1}. The critical speed in tension permits an estimate to be made of the diffusion coefficient of N_2 into the polymer at 78.

Publications:

Brown, N. and Fischer, S., "Nucleation and Growth of Crazes in Amorphous Polychlorotrifluoroethylene in Liquid Nitrogen", J. of Polymer Sci. 13, 1315 (1975)

Brown, N. and Imai, Y., "The Yielding of Polycarbonate in a Nitrogen Environment at Low Pressures and Temperatures", J. Poly. Sci. Lett. (Accepted)

Brown, N. and Parrish, M. F., "Environmental Crazing and Fracture of Polymers in Nitrogen, Argon, and Helium", Recent Advances in Science and Technology of Materials, Ed., A. Bishay, Plenum Press, Vol. 2 (1974) p. 1

Mindel, M. J. and Brown, N., "Creep, Recovery and Fatigue in Polycarbonate", J. of Mat. Sci. 9, 1661 (1974)

Treharne, R. W. and Brown, N., "Factors Influencing the Creep Behavior of Poly(methyl Methacrylate) Cements", J. Biomedical Materials Res. Symp. No. 6, 81 (1975)

2. Structure and Properties of Polymers

W. C. Forsman, Associate Professor of Chemical and Biochemical Engineering

Postdoctoral Fellow: S. K. Poddar

Research Assistant: Y-S. Ko

Support: NSF-MRL
NIH

Objective and Approach: Materials based on polymers have found a broad spectrum of applications ranging from surgical implants to the high-performance composites (fiber filled polymers) used as structural members in aircraft. Furthermore, polymers in solution are used in important applications ranging from flocculants for pollution control, to rheology control agents in the water flood process for tertiary oil recovery.

The performance of polymer-based materials and how easily they can be fabricated ultimately depends on two factors -- molecular structure of the polymer and how the polymer molecules interact with their environment. The behavior of polymers used in solution is a function of molecular structure, polymer-polymer and polymer-solvent interactions. The broad goal of our research is to contribute to the body of knowledge of how molecular structure and polymer interactions relate to the application of polymeric systems.

Progress:

A. Development of High-Frequency Rheometer

A Rheometer has been developed in this laboratory to study the linear viscoelastic behavior of liquids and solutions at 80 KHz. For polymer solutions this frequency is high enough to be associated with the response of polymer molecules in short blocks of the chain backbone. The apparatus may be used for solutions having viscosity as low as about 2 c. p. Until now, no similar instrument has been reported in the literature which is suitable for measuring the high-frequency viscoelastic behavior of solutions (or simple liquids) having dynamic viscosities in this range. Furthermore, the instrument is capable of determining G' and G'' to values as low as 10^3-10^4 dynes/cm^2. The accuracy of G' and G'' does, however, fall off dramatically below 10^3 dynes/cm^2.

Equations have been developed and a computer solution has been worked out for determining G' and G'' of the solvents and solutions. Unique calibration techniques for the instrument were also devised. The calibration

of the present apparatus is self-consistent. An added feature of the present equipment is its capability of detecting precisely the phase shift and attenuation of the different orders of reflection (up to the 8th order of reflection can easily be detected depending, of course, upon the type of liquid being tested).

B. Viscoelasticity of Aqueous Polyacrylamide Solutions as Function of Temperature and NaCl Concentration

Dynamic viscoelastic measurement of aqueous polyacrylamide solution was carried in the low frequency region (2×10^{-2} to 2×10^{2} rad/sec) using Model R-18 Weissenberg Rheogoniometer. This work was supplemented by measurements using the high-frequency Rheometer described above. Experiments were performed on 2.5 and 3.5% aqueous polyacrylamide solutions between 5 and 40°C in distilled water and in 0.2 and 0.4 N Sodium Chloride solutions.

Both the series at 2.5 and 3.5% demonstrated the same type of behavior.

Both G' and G'' at 80 KHz show a transition between 10° and 20°C, and G' demonstrates a precipitous drop as T → 40°C. This is interpreted as competition between two phenomena - chain hydration and helical block formation (which is stabilized by intramolecular hydrogen bonding). This interpretation is consistent with the dynamic behavior demonstrated at low frequency as measured with the Rheogoniometer.

Our work represents a unique technique in establishing the relationship between chain solvation and conformation in moderately concentrated polymer solutions.

C. Chain Dimension and Dilute Solution Behavior of Poly(1,4-Dichloro-2,3-Epoxybutane)s

This research was a detailed examination of chain dimensions, polymer-polymer and polymer-solvent interactions of a highly sterically hindered polyether. Experimental work included intrinsic viscosity, light scattering, osmometry and gel permeation chromatography. Intrinsic viscosities were measured in N,N-dimethylformamide, N,N-dimethylacetamide and cyclohexanone between 10 and 80°C. Light scattering was measured only in N,N-dimethylformamide over the same temperature range and osmometry in the same solvent but only at 37°C.

The following conclusions were drawn:

1. The high value of the unperturbed chain dimensions in all the solvents suggests that the racemic diisotactic polymer exists in a helical block conformation in solution.

2. The proportionality of the unperturbed radius of gyration to the square root of the molecular weight indicates that the molecules behave as random flight chains even though the backbone is stiffened and probably exists in helical blocks.

3. The unperturbed radius of gyration of racemic diisotactic polymer is at least 1.41 and 1.33 times those of meso diisotactic polymer and (70-30 trans-cis) copolymer homologs respectively of the same molecular weight.

4. There is a transition temperature (in all the solvents) below which strong solvent-solvent interactions make it possible for the polymer to assume the stable helical block conformation. As the temperature is increased through the transition the weakened solvent-solvent interaction allows the solvent molecules to interact with the polymer disrupting the helical blocks. Further increase in temperature weakens the polymer-solvent interactions and the chain reverts again to the helical block conformation.

5. In each of the three solvents, for temperatures below the above-mentioned transition temperature, plots of RSV vs concentration show breaks at about 0.2-0.3 gm/dl concentration. We interpret this behavior to be associated with strong intermolecular polymer-polymer interaction (possibly even association) for those temperatures which also show strongest intramolecular polymer-polymer interaction.

6. Consistency between all aspects of light scattering and intrinsic viscosity results offers evidence for the applicability of various theories used for interpretation, namely Flory-Fox viscosity equation and Stockmayer-Fixman technique for treating the excluded volume effect.

7. The good agreement between the Z-average radius of gyration predicted from intrinsic viscosity and the observed values from light scattering suggests that the Schulz-Zimm distribution is an adequate representation of the molecular weight distribution of the racemic diisotactic polymer.

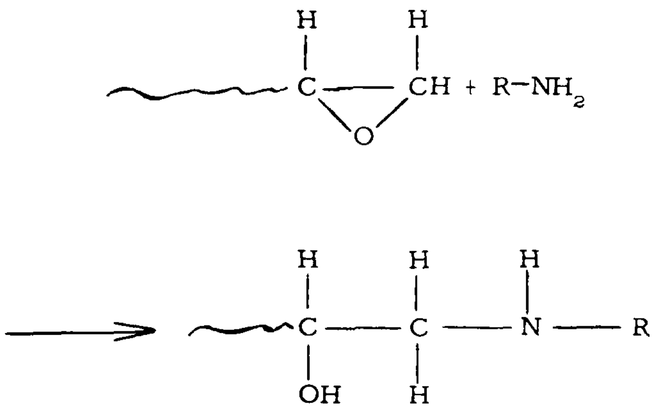
8. Intrinsic viscosity-temperature behavior of the meso diisotactic polymer and (70-30 trans-cis) copolymer are qualitatively similar to that of racemic diisotactic polymer. This suggests some degree of ordering in these two polymers as well. But detailed interpretation would require considerably additional experimental work. This detailed dilute solution study illustrates many of the complexities in polymer-solvent and polymer-polymer interactions in even moderately polar systems, most of which have never before been separated.

D. Graphite-Epoxy Composites

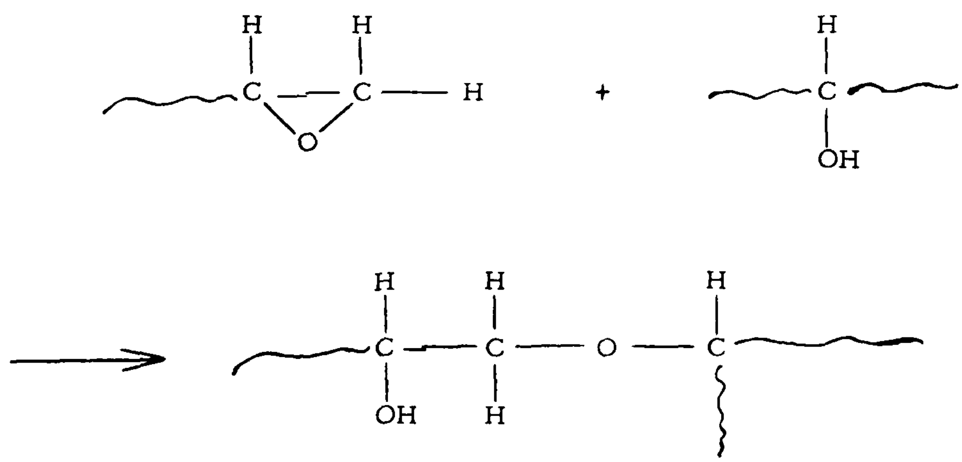
This report phases out our LRSM support for research on polymer-carbon fiber composites. We have been studying the linear viscoelastic

behavior of both composites and cast polymer specimens as functions of temperature, composition and fiber surface treatment with a focus on the polymer-fiber interface.

We have found that better heat resistant composites can be made using non-stoichiometric epoxide polymer matrices. The stoichiometric polymerization reaction is



With excess epoxy, we postulate the following secondary reactions also take place:



This secondary polymerization can be monitored by rubbery behavior above the glass transition and by the disappearance of an internal friction peak at 60°C. We postulate that it is this secondary polymer network that is responsible for the higher modulus at room temperature and the 20°C elevation of the glass transition.

In addition, we have established that there is a reversible change in fiber-polymer interaction in the presence of H_2O. This breakdown in interfacial bonding is detected by internal friction measurements (determined with our modified Weissenberg Rheogoniometer.)

Publications:

Gupta, S. K. and Forsman, W. C., "Statistics of Branched, Random-Flight Chains", Macromolecules 7, 853 (1974)

Gupta, S. K., Shah, V. R. and Forsman, W. C., "Molecular Relaxation of Nearly Monodisperse Polystyrene Melts", Macromolecules 7, 948 (1974)

3. Theory of Metallic Cohesion

L. A. Girifalco, Professor of Metallurgy and Materials Science

Research Assistant: R. Kalkan

Support: NSF-MRL
AFOSR

Objective and Approach: The purpose of this work is to apply the theory of metallic cohesion to metallurgical phenomena such as alloying, defect formation and fracture, using localized wave functions. In the current phase of the work, the energy of solution of an impurity atom in a host crystal is being computed using our recently developed generalized Wannier formalism. It is assumed that the Wannier-Lowdin orbitals for each atom depend only on density, but are otherwise rigid. Atomic relaxation effects are taken into account via the Kanzaki lattice statics method. The importance of this work is that, if successful, it will provide a new, straightforward methodology for defect and alloy energy studies that is more soundly based than those commonly used. Since so many metallurgical phenomena depend on local atomic interactions, a localized wave function method should find extensive application.

Progress: To date, the following parts of this program have been completed:

1. The cohesive energy formalism has been transformed into localized Wannier form, and has been generalized to non-periodic as well as periodic systems. The Wannier one-electron theory (as developed by Koster and Slater) has also been generalized to non-periodic systems, so that a complete theory with localized wave functions is available for crystals, liquids and amorphous solids, as well as defects.

2. The theory has been applied to the cohesive properties of the alkali metals, alkaline earths and cadmium (theory of cohesive energy, compressibility, lattice parameter and equation of state) with satisfactory results. This shows that the theory provides a practical tool that is comparable to more conventional methods.

3. It has been shown that assuming that the Wannier functions of each atom are rigid (i. e., independent of the surrounding atoms, except for changes in average density) gives a good representation of the redistribution of electrons around a vacancy. If this "rigid pseudoatom model" is valid in other kinds of defects, it will provide a powerful and simple method of studying the energetics and electron distribution of local regions in a metal.

In the current phase of the work, the energy of solution, and the local atomic positions are being computed for an impurity atom in a host crystal.

The basic assumption in the calculations is that the Wannier functions attached to each atom are rigid.

The methodology consists of computing the energy of the system from the unit cell and pair-wise cell-cell interactions of the generalized Wannier formalism, performing lattice sums to get the total energy. Atoms surrounding the impurity are allowed to relax in a manner restricted by symmetry requirements and the configuration of minimum energy is found by the Kanzaki lattice statics method. We have just completed the computer program, which is now being debugged, and results should be available shortly.

The immediate result of this work will be a picture of the distortion of the atomic environment around an impurity, and the energy of solution at infinite dilution, which can be compared to experiment.

The value of this work goes far beyond the specific results, however. A critical problem in point defect and impurity theory has been the proper analysis of the relaxation of both the electronic distribution and the atomic position. Traditionally, these are treated separately. The atomic positions are found by minimizing the lattice energy using a rigid two-body potential, the electron redistribution being neglected. The electron redistribution is usually studied by assuming all atoms remain at fixed lattice positions, and using simple one-electron or generalized Thomas-Fermi theory. In the present theory, both the atomic and the electronic redistribution are included simultaneously. The rigid Wannier function assumption results in a total electron density that varies with the atomic positions. A comparison of the resulting electron density with Thomas-Fermi theory and with integration of the Schrodinger equation for the vacancy case has been made. The results were very similar and support the rigid Wannier function model.

Also, the interatomic potentials used in our work are direct quantum mechanical results, in contrast to the empirical potentials commonly used.

We are also in the process of extending our work to more concentrated alloys in a program designed to yield the free energy of random alloys as a function of composition. The purpose of this is to understand the origins of alloying and solubility.

4. Cyclic Deformation and Fatigue Fracture

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Support: NSF-MRL
NSF
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ONR
ACC
GE
UEC

Objective and Approach: Premature failure of machines by fatigue has been a problem for over 100 years and even now over 90% of fracture-type failures are caused by fatigue. Although design approaches have improved greatly since World War II, incomplete understanding of the mechanisms of fatigue is one reason why extensive testing is still required to validate the design of a new structure. The aim of the work here is to provide a better understanding of these mechanisms. A complete understanding of fatigue in relation to the many variables which affect its mechanisms is beyond the resources of a single institution. Consequently, the following aspects have been selected for study: 1) hardening caused by cyclic stressing (and softening, which occurs in some materials), 2) crack nucleation processes, and 3) the relation between cyclic deformation and the kinetics of fatigue crack propagation. The approach is to employ mechanical testing of carefully controlled materials in conjunction with electron microscopy.

Progress:

1. Cyclic Deformation of Al-4% Cu Alloy Under Variable Loading

A pure binary alloy has been cycled under the variable loading mode of testing known as "incremental testing" since this has been shown, in a steel, to match cyclic deformation in a random spectrum test. The alloy was heat-treated to provide two types of microstructure broadly representative of many useful materials: 1) those containing small closely-spaced precipitates which can be cut by dislocations on plastic straining and 2) those containing larger precipitates impenetrable by dislocations. The first type

of microstructure showed a cyclic response, under incremental testing, essentially similar to that under constant amplitude cycling at equivalent strains, and cyclic softening even occurred at roughly similar accumulated strains. The second type give cyclic flow stresses 10 to 20% lower than those observed under constant amplitude testing at equivalent strains. Explanations for this behavior have been obtained from dislocation arrangements observed by electron microscopy.

2. Cyclic Deformation of Al-Zn-Mg-Alloy

In extension of the studies on pure binary alloy described above, the cyclic deformation of six commercial and experimental Al-Zn-Mg alloys has been explored. The alloys all have roughly equivalent Zn and Mg additions, and have been heat-treated for maximum hardness. They differ, however, with respect to additions of Fe, Si, Mn, Ti and Cr which are used to control the "constituent" particles and "dispersoids". Unlike the binary Al-Cu alloy, these Al-Zn-Mg alloys do not undergo cyclic softening. The main reason for this behavior is that the deformation is homogenized by the constituent particles.

3. Fatigue of a Ferroelastic Material

In order to understand the role of reversible plastic strain in fatigue, a ferroelastic alloy, Cu-15%Al-3% Ni (which undergoes reversible plastic strain on account of a martensite reaction) was cycled in pulsating compression. The material was chosen to be poly-crystalline. Complete control of the martensite reaction was achieved with difficulty, partly because the alloy of interest is very sensitive to precipitation during the betatizing quench. Testing was carried out in a range of temperature where the deformation was either ferroelastic or of regular slip. Failure occurred by an intergranular mode of cracking, and Coffin-Manson behavior was observed irrespective of the type of deformation. Studies using single crystals of the alloy are in progress.

Publications:

Calabrese, C. and Laird, C., "Comments on Cyclic Response of Two Phase Alloys", Mat. Sci. and Eng. 15, 95 (1974)

Calabrese, C. and Laird, C., "High Strain Fatigue Fracture Mechanisms in Two Phase Alloys", Met. Trans. 5, 1785 (1974)

Finney, J. M. and Laird, C., "Strain Localization in Cyclic Deformation of Copper Single Crystals", Phil. Mag. 31, 339 (1975)

Kang, S. K. and Laird, C., "Precipitation in Thin Foils of Al-4w/o Cu Alloy, I: Morphology, Crystallography and Interfacial Structure of θ Precipitates", Acta Met. 22, 1481 (1974)

Kang, S. K. and Laird, C., "Precipitation in Thin Foils of Al-4w/o Cu Alloy, II: Growth Kinetics of θ Precipitates", Acta Met. 23, 35 (1975)

Laird, C., "Alloy Design for Fatigue Resistance", ASM Materials Science Symposium, Oct. 1974, Eds., G. S. Ansell and J. K. Tien, ASM (Accepted)

Laird, C., Chapter on "Electron Microscopy" in Characterisation of Solid Surfaces, Eds., P. F. Kane and G. B. Larrabee, Texas Inst. Co., Inc. (1974)

Laird, C., "Cyclic Deformation of Metals and Alloys", in Plastic Deformation of Materials, Ed., R. J. Arsenault, Academic Press (Accepted)

Laird, C., Finney, J. M., Schwartzman, A. and de la Veaux, R., "History Dependence in the Cyclic Stress-Strain Response of Wavy Slip Materials", J. Testing and Evaluation (Accepted)

Sankaran, R. and Laird, C., "Antiphase Domain Boundaries within θ' and η Precipitates", Mat. Sci. and Eng. 15, 159 (1974)

Sankaran, R. and Laird, C., "Effect of Trace Additions of Cd, In and Sn on the Interfacial Structure and Growth Kinetics of θ' Plates in Al-Cu Alloy", Mat. Sci. and Eng. 14, 271 (1974)

Sankaran, R. and Laird, C., "Interfacial Structure of Platelike Precipitates", Phil. Mag. 29, 179 (1974)

Sankaran, R. and Laird, C., "Kinetics of Growth of Platelike Precipitates", Acta Met. 22, 957 (1974)

Sankaran, R. and Laird, C., "The Role of Intruder Dislocations in Modifying the Misfit Dislocation Structures and Growth Kinetics of Precipitate Plates", Met. Trans. 5, 1795 (1974)

5. The Structure and Properties of Amorphous Alloys and Their Crystallization Products

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Research Assistants: S. Takayama
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Support: NSF-MRL

Objective and Approach: The amorphous metallic alloys constitute a most interesting material. For example, their fracture characteristics are nearer those of glasses rather than metals but unlike glass, they show deformation characteristics of metals. Our studies have shown that a predominant characteristic responsible for the amorphous alloy behavior must be the viscosity. There are, of course, many other fascinating reasons why this system of materials is of scientific interest. Our crystallization products are, themselves, of interest in the way they are transformed and in their mechanical behavior.

Progress: The phase transformations of amorphous alloys $Fe_{83}P_{10}C_7$ from the amorphous state to the crystalline state was studied by DSC which revealed a curie temperature at 325°C, two overlapping heat evolution peaks starting at 445°C and a third peak at 510°C. After the first heat evolution, (peak I), the sample was found to have been transformed to a metastable state along with αFe, Fe_3P and Fe_3C. The second peak was tentatively assigned to the growth of Fe_3P. The stable phases αFe, Fe_3P and Fe_3C are observed after the third peak. The activation energies for peak 1, 2, and 3 are 66, 64.6 and 65.7 Kcal/g mole respectively. The heat of transformation for the first and second peak are 880 cal/g mole and 120 cal/g mole respectively. The activation energies are 80 Kcal/g mole and 78 Kcal/g mole respectively.

The crystallization of $Ni_{55}Pd_{35}P_{10}$ alloys was examined by isochronal resistivity and hardness measurements, along with observations of the phase transformation in the heating stage of a transmission electron microscope (T. E. M.). The resistivity temperature coefficient between 26 C and 250 C is low (9.38×10^6 /°C); a few metastable phases form on crystallization. The hardness-temperature curve shows the hardness to increase as the metastable phases appear.

Ni-Pd-P amorphous alloys show an inhomogeneous plastic deformation as do all other amorphous alloys. A few localized deformation bands appear macroscopically just beyond the elastic region of the stress strain curve. In most cases, ribbon samples fracture in a plane stress condition

and in an antiplane shear mechanism (mode III). It is also revealed that two types of localized deformation bands can be produced during tensile deformation, i.e., one has sharp steps which are produced by plastic flow associated with a shear, and the other has interconnecting voids similar to a crazing crack in polymers.

Coordinated resistivity and stress-strain measurements of $Ni_{55}Pd_{35}P_{10}$ and $Ni_{63}Pd_{17}P_{20}$ amorphous alloys were conducted at liquid nitrogen temperature. These measurements show that a small deviation in the electrical resistivities occurs prior to the 'apparent yield' on the stress-strain curve. It is suggested that this phenomenon is associated with an atomic displacement below the elastic limit of the material.

Thickness reduction, ϵ_T, and the elongation of Ni-Pd-P metallic glass up to 26% and 40% can be obtained in rolling. Deformation bands develop and are wavy in appearance and similar to single crystals of pure B. C. C. metals. Observations at various stages during bending show that cracks can be created as the result of the crossing of two 'slip bands' similar to the behavior in crystalline materials.

Mechanical behavior, deformation and fracture were investigated on $Ni_{55}Pd_{35}P_{10}$ and $Ni_{63}Pd_{17}P_{20}$ amorphous alloys made by an improved Pond and Maddin method. The stress-strain curves of Ni-Pd-P amorphous alloys show a quasi-brittle behavior with an average fracture stress of $Ni_{55}Pd_{35}P_{10}$ and $Ni_{63}Pd_{17}P_{20}$ as 149 kg/mm^2 and 142 kg/mm^2 respectively. These stresses are quite high in comparison to normal metals and alloys. The elongations are small, 0.042% and 0.023% for $Ni_{55}Pd_{35}P_{10}$ and $Ni_{63}Pd_{17}P_{10}$ respectively (as in the elongation of all amorphous alloys). The observation of fracture surfaces made with a scanning electron microscope shows two distinct regions, i.e., 1) featureless parts called 'veins' or 2) 'ridge' patterns. A suggested grease model gives a good simulation of the actual fracture morphology. Deformation in a tensile stage in a transmission electron microscope shows that plastic zones appear at the crack tip in advance of the crack propagation.

Publications:

Maddin, R., "Early Iron Metallurgy in the Near East", Trans. Iron and Steel Institute of Japan 15, 2, 59 (1975)

Masumoto, T. and Maddin, R., "Structural Stability and Mechanical Properties of Amorphous Alloys", Mat. Sci. and Eng. 19, 1 (1975)

Takayama, S., "Amorphous Structures: Their Formation and Stability", J. Mat. Sci. (Accepted)

Takayama, S. and Maddin, R., "Fracture of Amorphous Ni-Pd-P Alloys", Phil. Mag. (in press)

Takayama, S. and Maddin, R., "Resistivity Changes by Deformation of Ni-Pd-P Amorphous Alloys", Scripta Met. 9, 343 (1975)

Takayama, S. and Maddin, R., "Rolling and Bending Deformation of Ni-Pd-P Metal Glasses", Acta Met. (Accepted)

6. Embrittlement of Structural Alloys by Impurities

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Support: NSF-MRL
AISI
NSF
NASC
PSEF
WRC
MPC

Objective and Approach: The overall objective of this research is to achieve a fundamental understanding of the embrittlement of structural alloys by impurities and to provide the basis for optimization of such alloys for toughness at ordinary and elevated temperatures and in aggressive environments. Elements from Groups IV to VI, the "metalloids", tend to segregate to grain boundaries in transition metals and to reduce cohesion there. This leads to a reduction in fracture toughness, often over a wide range of temperature, and to enhanced cavitation and cracking growth in grain boundaries at high temperatures. This also causes an enhanced sensitivity to intergranular cracking under stress in aggressive environments, the apparent result of an attractive interaction between metalloids and hydrogen (hydrogen-assisted cracking) and of the ability of metalloids to interfere with re-passivation after slip-induced oxide film rupture (stress corrosion cracking). The specific objectives of this program are: (1) to determine the embrittling potency of each important metalloid element; (2) to determine how the above actions of each element are influenced by changes in microstructural variables, such as hardness and grain size; (3) to determine the factors, such as alloy content and thermal history, which control the kinetics and equilibrium amounts of metalloid segregation (as a function of temperature).

The approach in this program involves: (1) correlation of notched-bar fracture energy with grain boundary composition, as measured by Auger

electron spectroscopy; (2) measurements of grain boundary and free surface segregation of metalloids as a function of alloy content, temperature, and time; (3) measurement of effects of individual impurities on cavitation and cracking in notched bars at elevated temperatures; (4) measurement of the effects of the metallic alloy elements on the thermodynamic activity in solution of metalloid elements; (5) investigation of the physical basis for reduction in cohesion by metalloid elements; (6) investigation by transmission electron microscopy of the modification of grain boundary microstructure as a result of embrittlement processes.

Within the past year we have achieved several important breakthroughs in this problem. We have finally worked out the relative importance of the various parameters, and in several areas we have moved beyond the exploratory stage to positions from which a directed research effort will systematically develop fundamental knowledge which will be directly transferable to practice in the optimization of resistance to embrittlement of alloy steels.

We have discovered that the tough-to-brittle transition temperature is a unique function of grain boundary concentration of any given metalloid impurity in a steel of fixed hardness and grain size, regardless of the aging time and temperature combination used to achieve that concentration. The embrittlement potential of each metalloid element shows up in the plot of transition temperature versus grain boundary concentration, and it is found that the potency increases with period number and group number in Groups IV A to VI A in the Periodic Table. In addition, we have found that, for a given grain size and grain boundary concentration of metalloid, the transition temperature is a strong, monotonic function of the hardness of the steel for each metalloid studied so far. From these results and prior work of Capus on the effect of grain size variation in steels of constant hardness and grain boundary composition, we have shown that plots of transition temperature versus grain boundary concentration, hardness, and grain size are sufficient to describe the degree of embrittlement of a steel.

The remaining work on the problem of embrittlement at ordinary temperatures can now be divided into two tasks; one is the determination of the embrittlement diagrams (as described below). The other involves the determination of the factors which control the amount of metalloid which will segregate to grain boundaries in any given steel. We have already determined some of these factors; for example, the level of Ni in the steel controls the activity of Sb, and the level of Ti and Mo can be used to control the activities of Sb and P. Our previous conclusions about the transitory nature of the embrittlement have been revised; further experiments now indicate that it may be better described as an equilibrium phenomenon controlled by matrix composition, but that the approach to equilibrium can be greatly accelerated by transitory phenomena, such as solute re-arrangement due to the precipitation of carbides in grain boundaries. Experiments on the

segregation of elements to a heated free surface in multi-component steels have shown that segregation of metalloids is strongly influenced by matrix composition; e.g., Mo suppresses segregation of P, and both Cr and Mo suppress segregation of S.

The net result is that we have demonstrated that it is possible to control the degree of embrittlement by the variation of several parameters and that this flexibility should permit the production of embrittlement-resistant steels. The experimental program over the next several years will, therefore, be concerned with the development of this general approach, as well as achieving fundamental understanding of the various important aspects of the phenomenon.

Publications:

McMahon, C. J., Jr., "Embrittlement of Alloy Steels by Impurities", Conf. on the Mechanics and Physics of Fracture, Churchill College, Cambridge, Jan. 1974

McMahon, C. J., Jr., "The Strength of Grain Boundaries in Metals and Alloys", Conf. on Grain Boundaries in Engineering Materials, Bolton Landing, N. Y., June 1974

Ohtani, H. and McMahon, C. J., Jr., "Modes of Fracture in Temper Embrittled Steels", Acta Met. (Accepted)

Rellick, J. R. and McMahon, C. J., Jr., "Intergranular Embrittlement of Iron-Carbon Alloys by Impurities", Met. Trans. 5, 2439 (1974)

Sessions, M. L. and McMahon, C. J., Jr., "The Influence of Stress Components on Intergranular Oxidation and Cracking in a Nickel-Base Superalloy", Conf. on Grain Boundaries in Engineering Materials, Bolton Landing, N. Y., June 1974

7. Mechanical Properties of Ordered Alloys

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E. Kuramoto

Research Assistant: D. R. DiMicco

Support: NSF-MRL
NSF-RANN

Objective and Approach: Ordered alloys are playing an increasingly important role in materials technology. (An ordered alloy is simply an alloy containing at least two kinds of atoms, A and B, in which the A atoms occupy specific lattice sites and the B atoms occupy other specific lattice sites.) Materials used at high temperatures, for example materials used in the manufacture of gas turbine blades, contain a large volume fraction of an ordered phase, Ni_3Al. Also alloys that can be deformed by large amounts and later return to their original shape exhibiting the so called "shape memory effect", are also ordered alloys.

Several ordered alloys exhibit remarkable strength increases with increasing temperature, just the opposite of ordinary alloys. They also can have rather high melting points and exhibit good corrosion resistance. However, alloys containing a significant volume fraction of an ordered phase tend to have rather limited ductility, i.e., they tend to be brittle. It is important to realize that the less desirable properties, like limited ductility, tend to reduce the available margin of error for a given application, so that the user of these sophisticated, specialized materials must have an equally sophisticated knowledge of their specific properties.

In this study I am using dislocation velocity measurements, yield stress and work hardening measurements, and electron and optical microscopy, trying to understand the origin of the increasing yield strength with increasing temperature, and the unusually high work hardening rate of alloys with the same crystal structure as Ni_3Al and Cu_3Au.

Progress: In the past year we have made progress in several areas. First we have made further efforts to test our ideas reported last year on the yield strength of Li_2 (ordered alloys with the Cu_3Au crystal structure) alloys. The ideas are consistent with all data currently available. The basic ideas for the yield strength theory were extended and we now believe we also understand the reasons for the unusual work hardening behavior of Li_2 alloys. (Work hardening is the process by which a metal gets increasingly difficult to permanently deform with increased deformation.)

The theory of work hardening in pure metals is currently not well developed because of the complexity of the problem. In Li_2 alloys the work hardening rate changes strongly with temperature and with crystallographic orientation, and furthermore the work hardening rate of polycrystalline material is much higher than that of single crystalline material. This is in general, not the case in pure metals. We are now in the process of growing Cu_3Au crystals of various orientations to check our ideas.

We have also made progress in our experiments on Ir_3Cr, and Li_2 alloy on which no previous yield stress experiments have been performed. Polycrystalline compression test samples have been produced (no easy task with a 2400°C melting temperature and drastically different vapor pressure of Ir and Cr) and compression tests have been performed between 600 and 1400°C (again, compression tests at 1400°C are rather difficult). Since these results are new and we haven't had time to digest their meanings, we would rather not comment on them now except to say that they seem to indicate that Ir_3Cr behaves quite differently from other Li_2 alloys we have tested.

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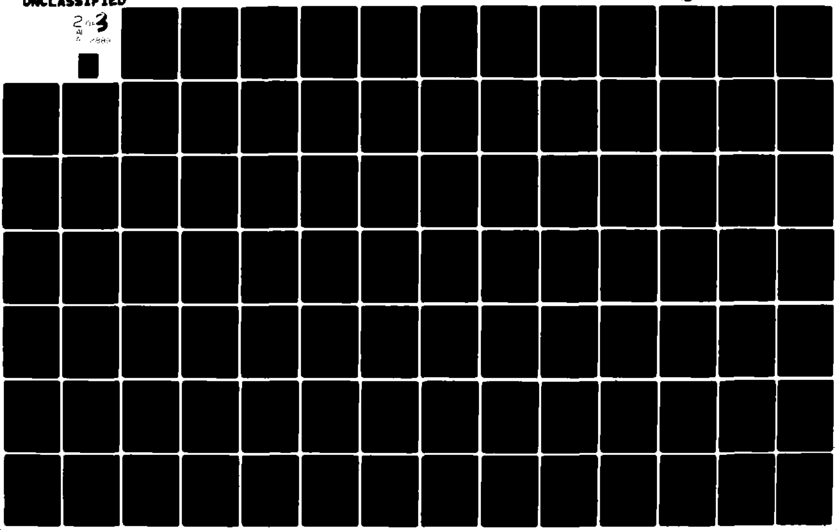

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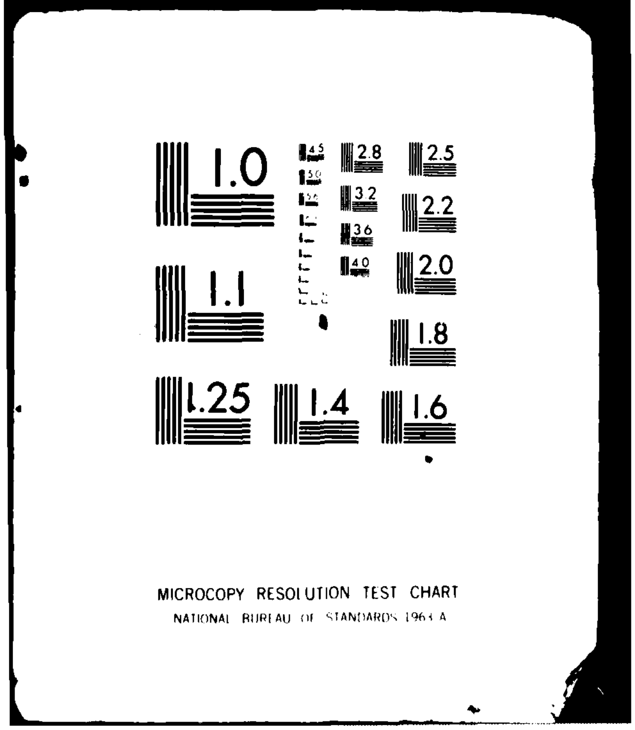
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D. CHEMICAL AND EXTRACTIVE METALLURGY

1. High Temperature Metallurgical Chemistry

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Support: NSF-MRL
NSF
AISI
ARPA-LRSM

Objective and Approach: The objective of this research program is to further our understanding of the mechanisms and complex equilibria which are involved in extraction and refining processes. The particular emphasis at the moment is on the gas-metal reaction and the slag-metal reaction with some initial work on slag-gas reactions. The experimental approach in gas-metal reactions is one of determining the rate-laws for decarburization and oxidation of liquid metals, particularly by CO_2, using electrochemical cell methods and continuous solute - replenishment steady-state weight loss techniques. Both approaches were developed in this laboratory. In the case of slag-metal reactions, the emphasis is on the use of chronopotentiometry as a tool for determining the ionic constitution of simple silicates when dilute solutes are added and the state of oxidation is controlled. Optical absorption in the ultra-violet is being used as a technique to study the extent of the defect state in the silicate anionic structure as a function of oxygen potential, it being thought probable that this is more important than previously thought and possibly responsible for the formation of metal fogs and losses in the slags of some refining processes.

A detailed understanding of the factors which influence the rates and equilibria of metallurgical processes will lead, in the long term, to better technological control and efficiency in energy requirements in the winning of metals for over use.

Progress: This has been a year of significant progress in the studies of gas-metal reactions. Experimental studies of the decarburization of liquid iron, under the conditions of continuous saturation with carbon, have established that the forward rate is proportional only to the pressure of CO_2. Rates have been found to be very much higher than previously reported in

the literature, it being now certain that such previous studies were in the region of gas-transport control. Additional work has now shown that the rate is <u>independent</u> of the carbon concentration of the iron, hence the rate controlling step is the dissociation of the adsorbed CO_2 on the surface of the melt. The rates and rate law have already permitted the rational interpretation of a number of apparently diverse studies in the reaction of carbon-saturated iron with slags and metallic oxides.

A tremendous sensitivity of the rates to the sulfur concentration has been found, particularly at the lower temperatures, 0.002 wt % S is sufficient to affect the rates at about 1300°C. A sensitivity to the group of metals, Sb, Sn, Pb has also been found.

Studies of the rate of deoxidation of liquid copper by carefully controlled shapes and sizes of graphites have shown that the rate is governed by the interfacial kinetics occurring at the gas film/metal interface. Reduction of CO_2 to CO by the graphite appears to be sufficiently fast to play no significant role by examining the effects of known catalysts for this reaction. The very precise electrochemical measurements have yielded rate constants which, on applying the principal of microscopic reversibility, agree well with other studies of the rate of oxidation of liquid copper by CO_2.

Theoretically, an ideal site-fillage isotherm has been developed to describe the depression of surface tension of liquid metals by surface active solutes. This isotherm is:

$$\sigma^P - \sigma = RT\Gamma_i^o \ln(1 + Ka_i)$$

where $\sigma^P - \sigma$ is the depression of surface tension of the pure liquid metal, Γ_i^o is the saturation coverage by the solute of bulk activity, a_i. The adsorption coefficient, K, is a coverage independent constant. The isotherm has been found to give a remarkably good description of the available data for Group VI solutes on liquid metals and to yield values of the adsorption coefficient which describe the interference of such solutes on interfacial reaction rates very closely, for those few interfacial reactions which have been studied.

Chronopotentiometric studies of molten silicates have been started and anodic transitions, tentatively ascribed to the O^{--} ion, have been reproducibly obtained at several compositions in the Na_2O-SiO_2 system. Cathodic transitions which have been observed elsewhere in experiments which were carried out in carbon containers have not been found in the present work (equilibrium with air). This already is in accord with the original supposition about the importance of a reduced state at very low oxygen potentials.

Publications:

Belton, G. R., Choudary, U. V. and Gaskell, D. R., "Thermodynamics of Mixing in Molten Sodium-Potassium Silicates", Physical Chemistry of Process Metallurgy, The Richardson Conference, I. M. M. London (1974) p. 247

Choudary, U. V., Serkin, J. A. and Belton, G. R., "A Mass-Spectrometric Study of the Thermodynamics of the Fe-Cu and Fe-Cu-$C_{(SAT)}$ Systems at 1600°C", Met. Trans. (Accepted)

Goldberg, D. and Belton, G. R., "The Diffusion of Carbon in Iron-Carbon Alloys at 1560°C", Met. Trans. 5, 1643 (1974)

Kim, Y-W. and Belton, G. R., "The Thermodynamics of Volatilization of Chromic Oxide: Part I. The Species CrO_3 and CrO_2OH", Met. Trans. 5, 1811 (1974)

Sano, N. and Belton, G. R., "The Thermodynamics of Volatilization of Chromic Oxide: Part II. The Species CrO_2Cl_2", Met. Trans. 5, 2151 (1974)

2. The Nature of Complex Oxide Melts

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Support: NSF-MRL
AISI
NSF

Objective and Approach: The objective of the project is the determination of the relationships which exist between the types of ions occurring in complex ionic melts and those thermodynamic and physicochemical properties of the melts which are, or could be, exploited in metallurgical processes.

The thermodynamic efficiencies of slag-metal refining reactions are determined solely by the activities of the slag components, which, in turn, are determined by the ions occurring and by the natures and extents of interaction among these ions. The limits of slag composition variation, and hence activity variation, within a slag system are determined by the positions of the various saturation surfaces. Such saturation occurs at critical values of pertinent ion activity products. Knowledge of the relationship between ion activity and interaction can, in principle, permit desired variation of saturation limits by suitable adjustment of ionic activities by means of minor solute additions. Similarly the performance of molten salt electrolytes in metallurgical electrolysis operations is determined by the influence of ionic form and interaction on such properties as electrical conductivity and transport number.

The approach being made involves comparison of the results of physical property, thermodynamic property and direct structural studies with the predictions of theoretical models of these systems.

Progress: A study of the possibility of determining the size range distribution of anions in silicate melts by extraction of the trimethylsilyl derivatives of the anions from quenched glasses has been completed. The experimental procedures were developed using specific crystalline silicate minerals known to contain only one type of silicate anion: for example, SiO_4^{4-} in olivine, $Si_2O_7^{6-}$ in hemimorphite and $Si_3O_{10}^{8-}$ in natrolite and boron phlogopite. The procedure involved extracting these ions from a powdered sample in acid aqueous solution as the corresponding silicic acid and then silylating the OH groups before condensation of the silicic acids could occur.

The silyl derivatives so produced were separated by gas chromatography and were identified by mass spectrometry. Although specific procedures were developed for efficient extraction of each ion type, it was discovered that experimental conditions for maximum yield of the monomer SiO_4^{4-} give a minimum yield of dimer $Si_2O_7^{6-}$ and vice versa. Thus, no unified procedure for efficient extraction of monomers and dimers from a single sample could be developed. Various compromise procedures were tried with quenched lead silicate glasses in the composition range PbO to $PbO.SiO_2$. Although qualitative indications of the size range distribution as a function of composition were obtained, it was concluded that accurate quantitative information could not be obtained.

Work is continuing on the thermodynamics of mixing in ternary silicate melts. Mixing in the liquid system Mn_2SiO_4 - Fe_2SiO_4 is being studied by equilibrating Mn-Fe foils with the mixed orthosilicate melts at 1450°C. Mass spectrometric determination of the thermodynamics of mixing in Pb-Sn silicates, Pb-Zn silicates and Sn-Zn silicates will be started on completion of the renovation of the time-of-flight mass spectrometer. Mixing in melts in the system MnO-SiO_2 - B_2O_3 is being studied by measurement of the activities of MnO and B_2O_3.

In an effort to identify a substitute for CaF_2 as the flux in basic oxygen steelmaking slags the effect of B_2O_3 on pertinent physico-chemical properties of CaO-FeO-SiO_2 melts are being studied. Initially the Ca_2SiO_4 saturation surfaces in the systems FeO-CaO-SiO_2-CaF_2 and FeO-CaO-SiO_2-B_2O_3 are being determined. This study will be extended to consider the relative effects of CaF_2 and B_2O_3 on melt viscosity.

Publications:

Agarwal, D. P. and Gaskell, D. R., "The Self Diffusion of Iron in Fe_2SiO_4 and $FeCaSiO_4$ Melts", Met. Trans. (Accepted)

Belton, G. R., Choudary, U. V. and Gaskell, D. R., "Thermodynamics of Mixing in Molten Sodium-Potassium Silicates", Physical Chemistry of Process Metallurgy, The Richardson Conference, I. M. M. London (1974) p. 247

Suito, H. and Gaskell, D. R., "The Reaction of Water Vapor with Melts in the System VO_2 - V_2O_5", Proc. of an International Symposium on Metal-Slag-Gas Reactions and Processes, The Electrochemical Society, 1975 (Accepted)

3. The Chemical Behavior of High Temperature Species

L. G. Sneddon, Assistant Professor of Chemistry

Research Assistants: M. Freeman
J. S. Plotkin

Support: NSF-MRL
RC
KCC

Objective and Approach: Over the past 30 years, a great deal of research has been conducted on the production and characterization of high temperature species formed by the evaporation of the solid elements and compounds. The species are, in general, extremely reactive and undergo chemical reactions not characteristic of the elements in the condensed phase at lower temperatures. Only recently have high temperature vapor species been used in synthesis, but preliminary results indicate that high temperature methods may be the synthetic and extractive methods of the future.

The basic technique consists of co-condensing the reactive high temperature vapor species with an appropriate ligand at a low temperature. The technique has the advantage that while the metal is a reactive high temperature species, the reaction with the ligand actually occurs at a very low temperature, thereby producing compounds which could not be produced in more conventional ways.

Besides its potential as a synthetic method, the technique also allows a unique way to study the reactivities of materials at high temperatures. Conventional high temperature studies have usually involved the reaction at a surface only. This new technique allows the formation and study of discrete compounds and should allow a determination of not only the final end product of a reaction, but should allow a trapping of intermediates produced.

The objective of the proposed research is to study the reactivities of high temperature species with a view to developing new synthetic and extractive processes.

Progress: Work has been initiated in the following areas:

1. Construction of a high temperature vaporization apparatus and an accompanying vacuum system is almost complete. This reactor will allow the vaporization of approximately 4-10 mmoles of metal vapor per hour and will be the basic apparatus used for the study of high temperature species. In addition to our studies on the reactions of metal vapors, we are also initiating an investigation of the high temperature reactions of metal sulfides using the same vaporization apparatus. Many metals are commonly found in nature as their sulfides, e.g., Fe, Co, Ni, Cu, Zn, Cd and Hg. These

elements are obtained from their ores with roasting followed by reduction of the oxide. It may be possible to develop alternative methods of processing these sulfides by studying their reactivities at elevated temperatures with a variety of inorganic and organic agents.

2. The reactions of other atomic species have been investigated. In particular, we have been interested in the reactions of sulfur atoms produced by the photolysis of sulfur-containing gases. Gunning and Strausz have shown that sulfur may be obtained as either singlet sulfur atoms (^1D) or in the ground state (^3P) by photolysis of carbonyl sulfide or carbon disulfide, respectively. These atomic species undergo a variety of insertion and addition reactions with parafins and olefins. We have found atomic sulfur species to be very reactive with inorganic compounds as well. We have produced the previously unknown compounds $C_2B_4H_6S$ and $C_2B_3H_5S$ by the reaction of sulfur atoms (^1D) with $C_2B_4H_6$ and $C_2B_3H_5$, respectively. We feel this technique may be an important new method for producing sulfur-containing materials, and we are expanding our research in this area.

Publications:

Greenwood, N. N., Savory, C. G., Grimes, R. N., Sneddon, L. G., Davison, A., Wreford, S., "Preparation of a Stable Ferraborane, $B_4H_6Fe(CO)_3$", Chem. Comm. 718 (1974)

Magee, C. P., Sneddon, L. G., Beer, D. C. and Grimes, R. N., "Bridge Insertion Reactions of the 2, 3-$C_2B_4H_5$-Ion with Aluminum Gallium and Transition Metal Reagents", J. of Orgmet. Chem. 86, 159 (1975)

Sneddon, L. G. and Lagow, R. J., "The Reaction of Lithium Vapor with Partially Halogenated Hydrocarbons", Chem. Commun. (Accepted)

4. Chemical Behavior of Materials at Elevated Temperatures

W. L. Worrell, Professor of Metallurgy and Materials Science

Postdoctoral Fellow: T. Sasa

Research Assistants: M. F. Brady
S-K. Lau
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Support: NSF-MRL
NSF
ARPA-LRSM

Objective and Approach: An understanding of the chemical behavior of materials in hostile environments is an essential requirement to improve the operation and efficiency of many high-temperature processes. The corrosion kinetics of nickel and nickel-chromium alloys in sulfur-oxygen atmospheres are being measured. The objective is to understand the fundamental corrosion mechanism, which will aid in the corrosion control of the gas turbines used for power generation and for propulsion of airplanes and ships.

A new class of exciting high-temperature materials are the exceptionally stable transition metal-platinum compounds, which should be excellent protective coatings for the transition metals in corrosive environments. To provide the fundamental information necessary to assess their usefulness, the coherence and kinetic properties of these compound coatings are being studied. These compounds are also important reaction products when platinum is used with refractory-metal oxides in high-temperature catalytic and fuel-cell applications. Kinetic investigations of several platinum-oxide (ZrO_2, Al_2O_3, Ta_2O_5) reactions are being performed to determine the rate and mechanism of compound formation as a function of temperature and oxygen pressure.

One major impediment in the development of useful energy-storage batteries is the lack of suitable positive electrodes (cathodes). Electrochemical-cell investigations using intercalated transition-metal sulfides (i.e., Na_xMS_2 as cathode materials are being continued. To evaluate quantitatively the potential applications of these intercalated sulfides, thermodynamic and kinetic data are being obtained. Electrochemical cell techniques are also being used to develop new solid electrolytes which have exciting possibilities as electrochemical sensors for sulfur and carbon.

Progress: Kinetic measurements of the corrosion of nickel in SO_2/O_2 atmospheres between 500 and 600°C have been continued. Using X-ray

diffraction, scanning electron microscopy, the electron microprobe and light microscopy, the morphology of the corrosion product layers has been characterized. Three product layers have been observed: adjacent to the nickel is a Ni_3S_2 layer, then a NiO layer, which is in turn covered by an outer "mixed layer" consisting of both Ni_3S_2 and NiO. The measured corrosion rate follows the parabolic rate law, which indicates that a diffusional process is the rate-controlling step. These results provide the first quantitative picture of the kinetics for such a complex gas-solid corrosion reaction.

Our experimental measurements of thermodynamic data in the Pt-Ti, Pt-Zr and Pt-Hf binary systems have been completed. Results confirm that intermetallic compounds ($TiPt_3$, $ZrPt_3$, $HfPt_3$) in these systems are exceptionally stable. Our measured values for the chemical stabilities of these compounds agree with the predictions of the Engel-Brewer correlation between electronic configuration, phase stability and crystal structure of alloys. Such thermodynamic data are essential for the quantitative assessment of the chemical behavior of these compounds at elevated temperatures and in various environments. Kinetic investigations of the platinum - Ta_2O_5 reaction indicate that the reaction rate is controlled by diffusional processes in the platinum-rich solid solution.

To aid in the development of solid-state electrochemical cells, kinetic studies of silver transport between a silver sulfide (Ag_2S) electrode and a AgI electrolyte have been carried out at 200°C using cell (A).

$$Ag,\ Ag_2S/AgI/Ag_2S \qquad (A)$$

Potentiostatic experiments confirmed that the chemical diffusivity of silver in Ag_2S is exceptionally high and that the overvoltage of cell (A) during current flow is extremely small. For example, an overvoltage of 5 mv is measured when the current density is 65 ma/cm^2. Such low overvoltages indicate that Ag_2S would be a useful electrode material. However, at current densities above 100 ma/cm^2, silver whiskers form at the electrolyte-cathode interface. Such whisker formation prevents cell recycling, which is essential for practical energy-storage cells.

Publications:

Meschter, P. J. and Worrell, W. L., "Evaluation of an NbO, $Nb_2O_{4.8}$ Reference Electrode for Emf Measurements at Low Oxygen Activities", Met. Trans. 6, 345 (1975)

Worrell, W. L., "Developing New Electrochemical Sensors", Proc. of the Int. Symposium on Metal-Slag-Gas Reactions and Processes, Electrochemical Society Meeting, Toronto, Canada; May 11-16, 1975 (Accepted)

Worrell, W. L. and Ramanarayanan, T. A., "Limitations in the Use of Solid-State Electrochemical Cells for High-Temperature Equilibrium Measurements", Cand, Met. Quarterly 13, 325 (1974)

Worrell, W. L. and Ramanarayanan, T. A., "Overvoltage Phenomena in Oxygen-Saturated Copper Electrodes", Met. Trans. 5, 1773 (1974)

Worrell, W. L. and Ramanarayanan, T. A., "A Thermodynamic Investigation of Cubic Sodium Tungsten Bronze, Na_xWO_3", J. Electrochem. Soc. 121, 1530 (1974)

E. ELECTRONIC AND MAGNETIC MATERIALS

1. Raman, Optical and Acoustical Spectroscopy of Solids

E. Burstein, Professor of Physics

Postdoctoral Fellow: H. Talaat

Research Assistants: S. P. B. Buchner
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Support: NSF-MRL
ARPA-LRSM
ONR
AROD
U of P

Objective and Approach:

a. To study experimentally and theoretically the scattering of light by elementary excitations including surface excitations in order to elucidate the fundamental mechanisms of light scattering including the effects of finite wave vector and applied fields and to develop light scattering as a probe of the electronic properties of solids and of surfaces.

b. To study the linear and non-linear properties of surface elastic and electromagnetic waves which propagate along surfaces or interface of dielectric, metallic and magnetic media in order to elucidate the fundamental nature of surface waves and to develop surface wave spectroscopic techniques for the investigation of surfaces and interfaces.

Our short range goals are: i) to determine the relative roles played by finite wave vector and surface space charge electric fields in forbidden scattering by LO phonons in III-V compounds; ii) to elucidate the scattering of light by surface EM waves and related non-linear optical phenomena, i. e., second harmonic generation, parametric mixing, etc., involving surface EM waves, and iii) to explore the use of surface EM waves as EM probes of the vibrational and electronic excitations of chemisorbed atoms and molecules.

Progress:

1) We have shown, on the basis of our data on light scattering by the coupled LO phonon-plasmon modes in n-InAs at frequencies in the vicinity of the E_1 gap, that despite a sizeable scattering wave vector ($q \approx 5 \times 10^5$ cm^{-1})

and a high impurity density, the wave vector-dependent contributions to scattering within the skin depth are relatively small; and that the scattering by unscreened LO phonons that is observed in n- and p-type InAs is due to band bending at the surface. Using Raman scattering by LO phonons as a probe of surface space charge regions, we are investigating differences in the character of the space charge regions of (111) and (iii) surfaces of III-V compounds.

2) Using our theory of Raman scattering by surface polaritons, we have obtained values for the relative scattering, the relative scattering efficiencies of the surface and volume modes for an air | GaAs | Al_2O_3 layered structure which are in good agreement with the experimental data. We are now extending our theoretical analysis to the case of layered structures in which the slab is the non-linear medium, but not the surface-active medium and for which the scattering efficiency of the surface mode is determined primarily by the electro-optic contribution.

3) We have shown, on the basis of a detailed theoretical analysis, that there is an enhancement of the electric fields at metal/vacuum interfaces when surface EM waves are excited by prism (internal reflection) coupling, which is determined by $(L_s/\delta_v)^{\frac{1}{2}}$ where L_s is the propagation length of the surface EM wave and $\delta_v = 1/\alpha_v$ is the penetration depth of the surface EM wave in the vacuum. Under appropriate conditions, the normal and parallel components of the electric field of the surface EM wave at the interface are appreciably larger than their counterparts of the volume EM wave in an external reflection configuration. This electric field enhancement is largely responsible for the effective role played by surface EM waves in light scattering by rough surfaces and by gratings, in photo-emission and in second harmonic generation. In preliminary experiments, using surface EM waves excited by a prism-metal film - air configuration, we have obtained a marked enhancement of the fluorescence of very thin films of Rhodamine 6G over that for volume wave excitation. We are now investigating the possibility of using surface EM waves to observe Raman scattering by vibrational modes of molecular layers on metals.

Using a prism-silver film - air ATR configuration to couple volume and surface EM waves and a grating at the silver film, we have been able to observe the diffraction of the surface EM wave by the grating into volume EM waves in air and in the prism medium and the diffraction of a volume EM wave in air by the grating into a surface EM wave and the subsequent conversion of the surface EM wave into a volume EM wave by the prism. We have also observed the corresponding diffraction of volume and surface EM waves into one another using surface elastic waves at the silver film as a dynamical grating.

Publications:

Buchner, S. and Burstein, E., "Raman Scattering by Wave-Vector--Dependent LO-Phonon--Plasmon Modes in n-InAs", Phys. Rev. Lett. 33, 908 (1974)

Burstein, E., Chen, W., Chen, Y. J. and Hartstein, A., "Surface Polaritons: Propagating Electromagnetic Modes at Interfaces", J. Vac. Sci. and Tech. 11, 1004 (1974)

Chen, Y. J., Burstein, E. and Mills, D. L., "Raman Scattering by Surface Polaritons", Phys. Rev. Lett. 34, 1516 (1975)

Hartstein, A. and Burstein, E., "Observation of Magneto-Plasmon-Type Surface Polaritons on n-InSb", Solid State Commun. 14, 223 (1974)

Hartstein, A., Burstein, E., Palik, E. D., Kaplan, R., Gammon, R. W. and Henvis, B. W., "Optic Phonon-Magnetoplasmon Type Surface Polaritons on n-InSb", Int. Conf. Phys. Semicond; Stuttgart 1974 (Teubner, Stuttgart, 1974) p. 541

Mills, D. L. and Burstein, E., "Polaritons: The Electromagnetic Modes of Media", Reports on Progress in Physics 37, 817 (1974)

Pinczuk, A. and Burstein, E., "Fundamentals of Inelastic Light Scattering in Solids", Ed., M. Cordona (Springer Verlag) (Accepted)

Shand, M. L., Ching, L. Y. and Burstein, E., "Raman Scattering by Optical Phonons and Polaritons in CuCl", Solid State Commun. 15, 1209 (1974)

Talaat, H. and Burstein, E., "Phase-Matched Electromagnetic Generation and Detection of Surface Elastic Waves on Nonconducting Solids", J. Appl. Phys. 45, 4360 (1974)

2. Magnetic Bubble Materials

H. B. Callen, Professor of Physics

Support: ONR

Objective and Approach: In our general study of the physical properties of magnetic bubble materials we have concentrated on anisotropy, effects of disorder, and dynamic effects. This progress report focuses on a specific result obtained in the study of dynamic effects accompanying the motion of domain walls. In practical terms this work bears directly on the motion of "bubbles" and on the feasibility of bubble memories. In more fundamental terms it elucidates the magnetic response and fluctuation effects in magnetic materials.

Progress: We have completed an analysis of the "error generation" in bubble memories. The data giving rise to this work are striking and puzzling. The spontaneous annihilation of bubbles, due almost certainly to local magnetic fluctuation effects, is a logarithmic function of the time. Simple models of independent events predict an exponential dependence. We have shown that an interaction among bubbles, mediated by remanent effects, provides a mechanism for the observed data. This work thereby provides a basis on which reliability of bubble memories can be materially improved.

3. Perturbed Angular Correlation Study of the Hyperfine Interactions in Rare Earth Garnets

M. E. Caspari, Professor of Physics

Research Assistant: D. J. Bellafiore

Support: NSF-MRL

Objective and Approach: The technique of γ-γ perturbed angular correlations (PAC) was used to study the magnitude and symmetry of the magnetic and electric hyperfine interactions and the associated relaxation mechanisms in the rare-earth garnets. The garnets are insulators whose magnetic character can be varied from diamagnetic to ferrimagnetic by appropriately choosing the chemical components. By introducing the radioisotope, upon which PAC measurements can be made, into the garnet lattice either as an impurity ion or as a substitutional ion, a determination of the properties of the garnets can be made and the basic theories of magnetic interactions can be tested.

Previous PAC measurements performed on rare-earth ions in different garnets have neglected contributions from the lattice electric field gradient, the rare-earth rare-earth exchange field, and spin-spin relaxation because the observed effects were dominated by other mechanisms. These contributions were investigated by using radio-active $^{154}Gd^{3+}$ which is an S-state ion as a probe in various rare-earth aluminum and iron garnets as a function of temperature and applied magnetic field.

Progress: PAC measurements on $^{154}Gd^{3+}$ in yttrium aluminum garnet (YAlG), yttrium iron garnet (YIG), gadolinium aluminum garnet (GdAlG), and gadolinium iron garnet (GdIG) have been completed, and the results are being prepared for publication. The experimental data along with theoretical calculations indicate that a full description of the hyperfine interactions must include magnetic, electric, and relaxation effects. The observed behavior is best summarized by considering each of the above garnets.

A pure S-state ion introduced as an impurity into a diamagnetic host should exhibit a long relaxation time since spin-lattice and spin-spin relaxation mechanisms would be inoperative. An analysis of measurements on $^{154}Gd^{3+}$ ($L=0$, $S=7/2$, $J=7/2$) in YAlG in terms of a static magnetic hyperfine field due to the Fermi contact term and a lattice electric field gradient failed to explain the observed behavior. It was found, however, that good agreement between the experimental data and theoretical calculations could be obtained if the hyperfine interactions were allowed to be time-dependent. The measured relaxation times were on the order of 10^{-9} sec. This value can be attributed to the presence of magnetic impurities in YAlG leading to spin-spin interactions or the admixture of non-S character to the ionic description of the ground state of Gd^{3+} leading to spin-lattice interactions.

The presence of gadolinium spins in the host GdAlG immediately allows the electronic shell of the radioactive probe to relax via the Gd-Gd exchange interaction. As is to be expected, the analysis of the data requires a relaxation time which is faster than that found in YAlG but relatively slow compared to a typical non-S state rare-earth ion. The electrical field gradient produced by the surrounding ions was included in the final analysis.

Below the ferrimagnetic transition temperature in GdIG, the interactions between the ions are well described by exchange fields. These exchange fields, which act only upon the spin angular momentum of the ions, provide a local quantization axis and lift the degeneracy of the magnetic sublevels of the ionic ground state. A complete study of the problem revealed that the lattice electric field gradient, the time-average magnetic field due to the electronic configuration, the angle between the lattice electric field gradient and the effective magnetic field, and a relaxation time were necessary in order to explain the observed behavior. Above the Néel temperature, the data could be interpreted in terms of an electric field gradient and a relaxation parameter, with the result that the behavior of Gd^{3+} in GdIG was identical to that in GdAlG. This clearly demonstrates how important the presence of surrounding spins is to the consideration of relaxation effects.

A similar treatment of YIG indicates that the interactions of Gd^{3+} with its surroundings are different from those observed in GdIG with respect to the values of the relaxation times. The electronic shell of the Gd^{3+} ion was found to relax faster in YIG than in GdIG over the temperature range in which the description of the interactions depended mainly upon the relaxation parameter. This effect seems to indicate that the rare-earth rare-earth interaction of nonzero spins causes the ion under consideration to exchange magnons at a slower rate than that provided by the rare-earth iron interaction alone. The spin of the ionic probe in the case of YIG is free to follow fluctuations of the iron sublattice, but in the case of GdIG it must also follow the fluctuating rare-earth sublattice.

4. Amorphous Magnetism; Anisotropic Magnetic Materials

T. Egami, Assistant Professor of Metallurgy and Materials Science

Research Assistants: J. T. Prater
R. Williams

Support: NSF-MRL
ACC

Objective and Approach: The principal objective of this research program is to study and characterize various amorphous magnetic systems and to develop useful materials whenever possible. In addition, some anisotropic crystalline magnetic systems, mainly rare earth garnets, are studied using the high magnetic field facilities of LRSM.

As we have shown through this research program, certain amorphous alloys obtained by rapid quenching have excellent low-field magnetic properties which make them attractive as soft magnetic materials. Our main efforts are centered to further characterizing these amorphous alloys by various magnetic measurements and by structure study using the X-ray diffraction. In particular, factors which could influence the "amorphousness", such as chemical composition, heat treatment, mechanical deformation, and radiation damage, are carefully examined. The knowledge compounded during the course of this research may well result in improved performances of the alloys, or lead to the development of another property attractive for technological application - that is our long range goal.

The magnetic and structural studies are made also for magnetic oxide glasses and substitutionally disordered magnetic crystalline solids such as garnets, in order to investigate at a more fundamental level the effect of disorder on the magnetic properties of solids. Theoretical studies are carried out in an effort to relate the structure to the observed magnetic properties.

Along with the study of amorphous solids, research on crystalline magnetic materials pertinent to technological application is continued. In particular, we are studying the anisotropy and magnetization of garnets in high magnetic field, in collaboration with Bell Laboratory.

Progress:

Amorphous Magnetism

We have shown (with P. J. Flanders and C. D. Graham, Jr.) that some Ni-Fe amorphous alloys are excellent soft magnetic materials and could be used in devices such as transformers or strain sensors. Although the scientific interests in the amorphous magnetic materials have been

growing in recent years, the research has been largely theoretical or fundamental in nature. The realistic possibility of technological application of the amorphous magnetic materials were for the first time widely opened up by our work.

We found that the Ni-Fe amorphous alloys produced by Allied Chemical Co. have low coercivity (typically 0.06 Oe) and sizable remanent magnetization (2-3 k Gauss) and are good soft magnetic materials. Our major contribution however is that we found that these low field properties are significantly improved by the application of tensile stress, and the stress effect can be made permanent by annealing under stress. When improved (for instance coercivity 0.003 Oe remanence 4.9 k Gauss, or similarly 0.01 Oe and 8 k Gauss) the amorphous alloys compare favorably with the conventional crystalline materials such as permalloys. These findings resulted in three publications and three patent applications.

Researches in progress now are:

1) R & D effort to improve the a.c. performance of the amorphous alloy,
2) production of amorphous alloys with various chemical compositions,
3) structure characterization via X-ray diffraction - the energy dispersive X-ray diffractometer is under construction to perform high accuracy measurements,
4) preliminary work to investigate the radiation resistance of amorphous alloys,
5) low temperature high field magnetization measurement of transition metal oxide-phosphate glasses, and
6) theoretical calculation of static properties of random magnetic systems with finite single spin susceptibility.

Anisotropic Magnetic Materials

The field dependence of the magnetocrystalline anisotropy and magnetization of Yttrium-iron garnet (YIG) substituted by the light rare earth elements such as Pr, Nd, Sm, (Ho) are measured at 77 K in the field up to 68 kOe for anisotropy and up to 130 kOe for magnetization. The single crystals were prepared at Bell Lab. by the flux growth method. Many of the garnets were found to have unusually large field dependence of anisotropy which was qualitatively explained in terms of the crystal field effect. We are further extending this work to rare earth garnets diluted by Galium substitution, in order to study the effect of random magnetic dilution.

A theory to describe the dynamics of the spin system in high crystalline electric field via the thermal Green functions of spherical spin tensors was devised and was applied to S = 1 singlet ground state magnet. This is the first self-consistent calculation for this system, and has shown features

characteristic to the singlet ground state system, such as the mode-mode interaction, the k-dependent renormalization, and the soft mode at T_c. This effort is now largely completed.

Publications:

Brooks, M. S. S. and Egami, T., "Magnetic Anisotropy of the Heavy Rare Earths", AIP Conf. Proc. 18, 1258 (1974)

Brooks, M. S. S. and Egami, T., "Renormalization of the Magnon-phonon Interaction in HCP Ferromagnets", J. Phys. C; Solid State Phys. 7, 3594 (1974)

Egami, T. and Brooks, M. S. S., "Theory of Collective Excitation in Strong Crystal Fields", Proc. of the Conf. on Crystalline Electric Field Effect (Montreal, 1974) (Accepted)

Egami, T. and Brooks, M. S. S., "Unitary Transformation Approach to the Singlet Ground State Problem", AIP Conf. Proc. 18, 1300 (1974)

Egami, T., Flanders, P. J. and Graham, C. D., Jr., "Amorphous Alloys as Soft Magnetic Materials", AIP Conf. Proc. 24 (1975)

Egami, T., Flanders, P. J. and Graham, C. D., Jr., "Low-Field Magnetic Properties of Ferromagnetic Amorphous Alloys", Appl. Phys. Lett. 26, 128 (1975)

Flanders, P. J., Egami, T., Gyorgy, E. M. and Van Uitert, L. G., "Field Dependent Magnetic Anisotropy of Some Mixed Garnets with Light Rare Earths", AIP Conf. Proc., Magnetism and Magnetic Materials - 1974, Eds., C. D. Graham, Jr., G. H. Lander and J. J. Rhyne, AIP (1975)

5. Semiconductors: Defect States and Amorphous Materials

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S. Rabii, Associate Professor of Electrical Engineering and Science

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F. Sabet-Peyman
C. Y. Yang

Support: NATO
NSF
ARPA-LRSM

Objective and Approach: The behavior of crystalline semiconductors depends critically on the existence, energy distribution, and occupancy of defect and impurity states in the bulk, and on surface/interface states located where the specimen terminates or is joined to another material. These extrinsic states are responsible for many desirable properties, i.e., p-n junction formation. They also can be introduced inadvertently, i.e., atomic displacements due to exposure to nuclear or space radiation; interface states in MOS and heterojunction devices created during the fabrication process. Amorphous semiconductors exhibit many unusual and potentially useful properties; it is believed that all the states near the band edges are localized in space, analogous to bulk defect and surface states in crystals.

Our current understanding of intrinsic energy states is due to the applicability of many complimentary spectroscopic techniques for their complete characterization. The situation for extrinsic and disorder-induced phenomena has not matured as rapidly. To contribute toward this goal we will explore the above-listed aspects of imperfect semiconductor phenomena using modulated transmission spectroscopy as the primary experimental probe. The SCF-Xα-Scattered Wave technique will be used to study electronic states associated with defects in semiconductors, to elucidate their role in the electrical and optical properties and their response to chemical environment.

The same technique will be applied to the electronic density-of-states of amorphous semiconductors, and the degree of localization of band edge states for these materials will be investigated.

Progress:

A. The Self-Consistent Field-Xα-Scattered Wave Technique has developed into a powerful tool for the study of the electronic structure of molecules and localized states in solids. We have finished the development of an alternate full relativistic formulation which is based on the solution of Dirac's equation. This will furnish us with a fully relativistic description

of wave functions and spin-orbit-split electronic energies, without the need for perturbation calculations.

We have used a partially relativistic version of SCF-Xα-SW technique to explain the effect of atomic hydrogen on electrical properties of PbTe. The experimental results are consistent with our theoretical calculation for [H] Pb_3Te_4 cluster. Our results indicate that atomic hydrogen occupying the Pb vacancy reduces the number of holes associated with the vacancy by one.

Similar calculation on Pb_4S_4, [Pb vacancy] Pb_3S_4 and $CdPb_3S_4$ shows that, lead vacancy in PbS also introduces two holes. However, occupation of this vacancy by Cd completely reverses the effect by removing the two holes. These results are in general agreement with experiment but in a less direct and unique way as in the case of hydrogen in PbTe.

B. Amorphous silicon and germanium have been studied extensively. It had been hoped that the global features of topologically-disordered systems would be revealed in these "simple" materials, characterized by perfect "crystalline" short-range order but largely lacking correlations beyond second neighbors. A puzzling feature of previous results was the discrepancy between bandgaps inferred from optical and transport measurements; this discrepancy gave birth to the mobility gap. A notorious dependence of results on preparation and annealing history provided impetus for a cooperative series of <u>in situ</u> UHV experiments involving photoconductivity, DC conductivity and UV photoemission. Overlapping experiments were performed at China Lake, Stanford and Sandia, to insure reproducibility. A consistent picture has emerged from these experiments, namely an absence of localized states near the band edges (hence the mobility gap is equivalent to the denisty of states gap), and the inferred existence of a peak of localized states ~ 0.1 eV wide which pins the Fermi energy near mid-gap. The magnitude of the localized state peak is expected to be below the detectability limit of optical absorption and photoemission, so we have attempted to observe it using modulated absorption. Our first attempts employed electric field modulation; we envisioned a mechanism whereby the applied linear potential (10^5 V/cm) produces sufficient alteration in the random long-range atomic potential (10^6 V/cm or larger) to change the size and/or shape of the localized state peak, hence producing measurable change in absorption. These efforts have been unsuccessful to date. We will try thermoabsorption next; this should be particularly sensitive at ~ 240 K where the electron transport process changes from small-energy hops about E_f to thermally-activated conductivity in extended states.

Another aspect of the Penn program is directed toward the possible eventuality that the localized state peak doesn't exist. This would cast new doubt on the sharp absorption edge (which remains largely a matter of faith; the skeptics still being unconvinced). If the sharp edge is truly indicative of a density of states gap without appreciable band tails, then its magnitude must ultimately relate to the bond length, one of the few well-defined

quantities in amorphous semiconductors. Thus one expects deformation potential effects on the absorption edge associated with "lattice" dilation. Thermoreflectance gave a null result, which could in principle be due to a fortuitous cancellation between dilation and electron-phonon contributions. We are in the process of measuring Piezo-reflectance; a null result here would cast doubt on the entire sharp edge hypothesis and would require a new interpretation of the reliable, reproducible transport results.

Publications:

Donovan, T. M., Knotek, M. L. and Fischer, J. E., "Absorption and Transport Studies of Amorphous Ge", in Amorphous and Liquid Semiconductors, Eds., Stuke and Trenig, Halstead-N. Y. (1974) p. 549

Perov, P. I. and Fischer, J. E., "Thermoreflectance of TTF:TCNQ", Phys. Rev. Lett. 33, 521 (1974)

Rabii, S., "Effect of Strain on the Secondary Band Extrema of PbS, PbSe, PbTe, and SnTe", Phys. Rev. B7, 3830 (1973)

Rabii, S. and Lasseter, R. H., "Band Structure of PbPo and Trends in the Pb Chalcogenides", Phys. Rev. Lett. 33, 703 (1974)

Sood, A. K., Yang, C. Y. and Fischer, J. E., "Effect of Cl_2 Exposure on Thermoreflectance of Pb Chalcogenides", Thin Solid Films 16, 1 (1974)

6. Intercalated Graphite Compounds

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T. E. Thompson, Assistant Professor of Electrical Engineering and Science
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Postdoctoral Fellow: G. M. T. Foley

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Support: NSF
ONR
PSEF
ARPA-LRSM

Objective and Approach: The program has three ultimate objectives:

a) to synthesize graphite intercalation compounds with room temperature conductivities comparable to or even greater than that of copper;

b) to obtain sufficient understanding of the effects of intercalation on the electronic structure to guide the synthesis; and

c) to develop high-strength composite materials which will allow the practical realization of highly conducting intercalation compounds.

Progress: Our activities thus far have been directed toward establishing feasibility of the above objectives, learning how to intercalate with various acids, and assessing the suitability and usefulness of several experimental techniques. We report here the results of exploratory measurements which are being used to design the next, more systematic phase of the program. These results are summarized as follows:

1. Graphite fibers intercalated with nitric acid exhibit the same fractional conductivity increase as intercalated crystals (roughly a factor of 10). The elastic modulus increases slightly. These results offer promise of realizing a strong, highly conducting composite wire based on intercalated fibers.

2. Synthetic crystals intercalated with $BF_3 + F_2$ exhibit conductivity increases of 25x, the highest reported to date. This supports the simple idea that fractional charge transfer is correlated with the strength of acid, and suggests that intercalation compounds with room temperature conductivity greater than that of copper are feasible.

3. The metallic nature of acid intercalates has been confirmed by near IR reflectance spectra which exhibit free-carrier plasma edges. The

plasma frequency is higher for a superacid compound than for a HNO_3 compound, again suggesting stronger metallic character with superacid intercalation.

4. Graphite powders have been intercalated with SbF_5; powders are attractive because they are cheaper than fibers and because they are more nearly crystalline and thus offer hope of higher ultimate conductivity. A copper plus intercalated powder composite exhibits lower resistance than a piece of copper wire of identical geometry. The inferred conductivity of the compacted, intercalated powder is substantially greater than that of copper.

5. Room-temperature thermoreflectance spectra reveal several features suggestive of interband transitions, as well as a strong derivative response associated with the plasma edge. Strong critical point optical response is expected from singularities in a two-dimensional interband energy surface; these singularities are being analyzed to construct a zero-order band model for the intercalation compounds.

The first three results are discussed in detail below.

1. Intercalation of Fibers with HNO_3 (Vogel)

The starting material was Thornel 75 graphite fiber manufactured by Union Carbide Corporation. The initial resistivity was typically 6×10^{-4} Ωcm, although absolute values remain in question because of the difficulty in measuring the irregular and small (~ 6 μm diameter) cross sections. Thus greater reliance should be placed on the resistivity changes encountered rather than the absolute numbers.

The results of treatment of the Thornel 75 graphite fibers in red fuming nitric acid are shown in Table I for three temperatures of treatment. All resistivities were determined at room temperature. About an order of magnitude change occurs in intercalation, with the maximum occurring at the treatment temperature 57°C. From these results it is concluded that decreases in resistivity of the magnitude reported for graphite single crystals also occur in intercalated fibers.

Treatment Temperature °C	Resistivity (Ω-cm) Initial	Final	Ratio
80	8.5×10^{-4}	1.2×10^{-4}	7
57	8.0×10^{-4}	6.0×10^{-5}	12
27	6.1×10^{-4}	8.1×10^{-5}	8

Table I. Average resistivity change (at 295 K) for Thornel 75 fibers treated with HNO_3.

One matter of concern in contemplating the use of intercalated fibers in conductors is their mechanical properties, since many reports in the literature describe a loss of integrity or exfoliation with intercalation. Therefore the elastic modulus and tensile strength of Thornel 75 fiber were determined before and after intercalation with red fuming nitric acid. We found some diminution of tensile strength with treatment, although the effect is not large and can be considered unimportant since the tensile strength is so large to begin with. The elastic modulus, on the other hand, shows significant increases to values that are truly impressive. These results can be rationalized in terms of the strength being reduced by the etching out of macro defects by the acid and the modulus being increased by a reorganization of the crystal lattice caused by the intercalation process. These results augur well for the use of intercalated graphite fiber in composite materials.

2. Superacid Intercalation (Vogel)

A larger resistivity change than that produced by nitric acid resulted from treatment of the fiber in a gaseous mixture of fluorine and boron trifluoride. Results are shown in Table II. A three to one ratio of BF_3 to F_2 gave an average resistivity ratio of 14 when both the treatment and measurement were made at room temperature. The same treatment performed at 55°C resulted in a resistivity ratio of 25. This is a larger effect than any so far reported in the literature!

BF_3 Concentration	Temperature	Resistivity (Ωcm) Initial	Final	Ratio
75%	22°C	9.8×10^{-4}	6.9×10^{-5}	14
50%	22°C	8.5×10^{-4}	7.0×10^{-5}	12
25%	22°C	6.3×10^{-4}	1.3×10^{-4}	5
75%	55°C	2.1×10^{-3}	8.3×10^{-5}	25

Table II. Average resistivity changes in Thornel 75 due to intercalation with $BF_3 + F_2$.

If one uses the BF_3 ratio results to infer the effect on the a-axis resistivity of graphite single crystals, the resulting resistivity is $(4 \times 10^{-5}\ \Omega\text{-cm})/25 = 1.6 \times 10^{-6}\ \Omega\text{-cm}$, a value slightly lower than the resistivity of copper. This was confirmed experimentally by treating a sample of aligned graphite having an initial a-axis resistivity of $4 \times 10^{-5}\ \Omega$-cm (obtained from Union Carbide) with a 3/1 mixture of BF_3/F_2 for one hour at 55°C. The resulting a-axis resistivity was $2 \times 10^{-6}\ \Omega$-cm. This result must be considered preliminary due to difficulty in making voltage contacts to the aligned graphite after treatment.

3. Metallic Reflectance (Fischer, Thompson)

Plasma edges have been observed in the 300 K reflectance spectra of synthetic graphite intercalated with two acids. Soaking overnight in red fuming nitric acid at 23°C produces a stage 4 compound (c-axis repeat distance 13.8 Å) with the presumed chemical composition $(C_{96}^{+})(NO_3^{-} \cdot 3HNO_3)$ after a suggestion by Ubbelohde. The reflectance minimum occurs at 1.0 eV and the low frequency reflectance (0.2 eV) is 60-70%. Heating to 150°C in sealed tubes with a preweighed amount of SbF_5 leads to a weight gain of approximately 100%, from which we infer a composition $(C_{12}^{+})(SbF_6^{-})$, or approximately stage 1. The reflectance minimum of this latter compound is at 1.2 eV, and the low frequency reflectance is 80-90%, both indicating higher conductivity than the nitrate, consistent with the electrical measurements noted above. Analysis in terms of Drude theory is not justified at the moment due to the nonuniqueness of a 3-parameter fit and to uncertainties in the background dielectric function. Pure graphite should exhibit a reflectance minimum at 0.37 eV, but it is completely broadened out by the imaginary part of the background dielectric function associated with interband transitions. The mere existence of plasma edges in the compounds suggests gross shifts in E_f and/or major changes in band structure such that the threshold for interband transitions is much higher than in graphite.

Publications:

Aspnes, D. E. and Fischer, J. E., "Modulation Spectroscopy", in Encyclopedia Dictionary of Physics, Ed., J. Thewlis, Pergamon Press (Accepted)

Donovan, T. M., Knotek, M. L. and Fischer, J. E., "Absorption and Transport Studies of Amorphous Ge", in Amorphous and Liquid Semiconductors, Eds., Stuke and Trenig, Halstead-N. Y. (1974) p. 549

Fischer, J. E. and Aspnes, D. E., "Modulation Spectroscopy III. Band Structure Analysis", Comments on Solid State Physics 6, 39 (1975)

Loughin, S., Yang, C. Y., and Fischer, J. E., "On-Line Data Reduction with a Prism Spectrometer, Appl. Optics 14, 1373 (1975)

Perov, P. I. and Fischer, J. E., "Thermoreflectance of TTF:TCNQ", Phys. Rev. Lett. 33, 521 (1974)

Sood, A. K., Yang, C. Y. and Fischer, J. E., "Effect of Cl_2 Exposure on Thermoreflectance of Pb Chalcogenides", Thin Solid Films 16, 1 (1974)

Vogel, F. L., "Electrical Resistivity of Nitrate-Intercalated Graphite Fibers", Proc. 4th London Int'l. Conf. Carbon and Graphite (Accepted)

Vogel, F. L., "Implantation of Carbon in Thin Iron Films", Proc. 4th London Int'l. Conf. Carbon and Graphite (Accepted)

7. Relationship of Magnetic Properties to Structure in Selected Materials

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Research Assistants: D. A. Doane
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Support: NSF-MRL
NSF

Objective and Approach: Magnetic materials have been and continue to be of primary importance in a technological society. They are necessary for the generation and transmission of electric power, in many kinds of instruments and control devices, and in analog and digital information storage, handling, and processing. The development of new magnetic materials and the improvement of old magnetic materials requires (in addition to good luck and blind chance) an understanding of the ways that structure at various levels influences and controls magnetic properties.

The long-range goals of this program are broadly to learn more about magnetic properties and their control by structure, and to apply this knowledge to the improvement of existing materials and the development of new materials.

Major emphasis at present is on amorphous magnetic alloys prepared in ribbon form by the very rapid freezing of a liquid stream on a rotating drum. Such alloys can be made both amorphous and ferromagnetic over a wide range of compositions, are extremely strong mechanically, should be cheap to produce in quantity, and show (under proper conditions) d. c. permeabilities comparable to the best available crystalline alloys. They are potentially useful for all purposes now demanding permalloys and similar alloys, and perhaps for additional uses as well. The principal practical problem at present is low a. c. permeability, presumably resulting from too few domain walls and compounded by stress sensitivity.

A large number of interesting scientific problems have emerged, having to do mainly with the nature of the amorphous state, its changes with low-temperature annealing, and the resulting magnetic properties.

A second major interest in permanent-magnet materials, namely sintered $SmCo_5$ and directionally-solidified eutectic Bi-MnBi alloys.

Progress:

a. Plastic deformation of Dy crystals by high magnetic fi lds

This program is complete except for writing up the results for publication.

If ferromagnetic Dy in single-crystal form is subjected to high magnetic fields (above 75 kOe) along a magnetic hard direction (0001) at 4.2 K, a permanent plastic deformation of several percent may result. This phenomenon has been studied in detail. It is found that the deformation results principally from twinning, apparently caused by large magnetostrictive strains exceeding the elastic limit. Mounting the samples has been a major experimental problem, and the details of the deformation appear to be influenced by stresses due to the sample mount. Direct measurements of the slip and twinning systems on Dy have also been made for the first time. The effects of the mechanical twinning are reflected in the measured magnetic properties of Dy. This phenomenon will be of practical importance in any attempt to make use of the very high saturation magnetization of Dy at low temperatures.

b. Directionally-solidified Bi-MnBi eutectics

This is a joint project with Lehigh University. Some additional magnetic measurements have been made during this year; these generally confirmed earlier results. Major effort has gone into improved specimen preparation techniques, electron microscopy of samples to determine the phases present, and to the preparation of thin layers of pure MnBi by rf sputtering. Extensive magnetic measurement on new samples is planned for the summer of 1975.

c. $SmCo_5$ permanent magnets

Samples of commercially-made sintered $SmCo_5$ magnets have been obtained from the GE Research Center and from Hitachi M tals, Ltd. These cover a range of compositions and heat treatments, and therefore a range of magnetic quality. Measurements of magnetic anisotropy as a function of temperature are beginning, using the LRSM high-magnetic-field facility. The aim is to see if the anisotropy, an intrinsic magnetic property, correlates with the coercive field, a structure sensitive property. If so, the coercive field can be attributed to a simple domain-wall interaction effect.

Measurements on the elastic constants and magnetostriction constants of single-crystal $SmCo_5$ are complete, and the results are being prepared for publication.

d. Low-cost silicon solar cells

This is a project sponsored by NSF through the Center for Energy Management and Power. Participating are Prof. David Pope and Subhash Kulkarni, postdoctoral fellow. The practicability of hot-rolling polycrystalline silicon into thin sheets is being investigated. Polycrystalline cylinders have been successfully compressed by about 40% at temperatures near 1300°C in times of 10 to 20 minutes without failure, although some cracking has been observed. The samples appear to partially recrystallize during the deformation. The polycrystalline samples show highly anisotropic deformation. If further compression tests are encouraging, a high-temperature rolling apparatus will be constructed.

e. Amorphous magnetic alloy ribbons

Ribbons of four compositions, made by Allied Chemical Corp., have been extensively studied, both as straight ribbons and as toroidally-wound cores, with and without applied stress, and after various annealing treatments. Differential scanning calorimeter runs have been made to follow the process of crystallization, and some domain observations have been made. For some additional work, see the progress report of Takeshi Egami.

The situation at present may be summarized as follows:

The amorphous ribbons when measured as straight lengths under elastic tension have d. c. soft magnetic properties as good as or better than any available crystalline alloys. The elastic tension is necessary to overcome a small unfavorable magnetic anisotropy of unknown origin that presumably results from the manufacturing process. Annealing at about 200°C under an elastic stress or in a saturating magnetic field removes the unwanted anisotropy but tends to make the ribbons brittle (although not crystalline). The a. c. properties are substantially worse than would be expected from the d. c. properties, apparently because of a coarse domain structure that leads to high a. c. losses. This domain structure is not necessarily inherent in the amorphous materials.

Current efforts are devoted to:

1. Sample preparation, so that we are not dependent on Allied Chemical for samples. A high priority is being given to the production of alloys with zero magnetostriction.

2. Domain observations, both to aid in understanding the magnetic properties and to seek ways of reducing the domain size.

3. Correlation of magnetic anisotropy changes on annealing with the development of brittleness, to see if the two effects have a common origin.

4. Development of a treatment and/or composition that will give improved a.c. properties.

Publications:

Egami, T., Flanders, P. J. and Graham, C. D., Jr., "Amorphous Alloys as Soft Magnetic Materials", AIP Conf. Proc. 24 (1975)

Egami, T., Flanders, P. J. and Graham, C. D., Jr., "Low-Field Magnetic Properties of Ferromagnetic Amorphous Alloys", Appl. Phys. Lett. 26, 128 (1975)

Flanders, P. J., "Magnetostriction in Some Magnetic Oxide Compacted Powders", IEEE Trans. on Magnetics MAG-10, 1050 (1974)

Flanders, P. J., Graham, C. D., Jr. and Egami, T., "Magnetic Properties of Amorphous Alloys", IEEE Trans. on Magnetics (1975) (Accepted)

Ozawa, K., Flanders, P. J. and Graham, C. D., Jr., "Characterization of Magnetic Recording Tape with the Rotating-Sample Magnetometer", IEEE Trans. Magnetics MAG-10, 663 (1974)

8. Physics of Random Solids

A. B. Harris, Professor of Physics

Postdoctoral Fellow: W. K. Holcomb

Research Assistants: C. Dasgupta
R. Fisch

Support: NSF-MRL
NSF

Objective and Approach: We are studying a wide range of physical phenomena in random solids. Such properties include the nature of elementary excitations at low temperature, low temperature thermodynamics, behavior at the phase transition, and high temperature thermodynamics. From the standpoint of basic science it is obvious that the phenomenon of randomness can be important in almost all situations. The way underlying randomness in the Hamiltonian manifests itself could be an example of the occurrence of and importance of "hidden variables". This program unifies a number of different areas, notably magnetic phase transitions and behavior of alloys at the critical dilution where localized states give way to extended states. From a materials point of view it is clear that random alloys provide a new dimension of physical characteristics which may become important in various devices. At present our best understanding of dilution is in terms of small modifications from pure systems which are relatively well understood. Our program is focused on systems which can not be understood in such a simple way, but which require a totally new starting point.

Progress: An important advance in our understanding of the nature of and theoretical description of critical phenomena in random systems has been made in collaboration with Professor T. C. Lubensky. Our efforts have and will lead to calculations of increasing accuracy of the critical experiments in a wide class of random systems. We have already shown how to apply the renormalization group (RG) techniques to treat phase transitions in random systems. There we confirmed an earlier heuristic argument which predicted the criterion for randomness to modify the critical exponents.

Now we have applied RG methods to the percolation problem. In this problem sites are randomly occupied with a given average concentration, x, and the phase transition occurs at $x = x_c$ when the size of the largest connected cluster becomes infinitely large. Professor Lubensky is currently extending these ideas to treat a dilute magnet when the magnetic concentration x approaches x_c. Clearly, this class of problems for whose solution our work is essential, is a large one and is of wide interest.

In collaboration with Dr. S. Kirkpatrick of IBM we have calculated the elementary excitation spectrum of a number of random magnets. The important advance we have made is to show that the same hydrodynamic relations which are used in pure systems to relate dynamic quantities (such as sound velocities) to static properties (such as density or elastic constants) can be used to discuss the long wavelength low frequency excitations in dilute antiferro- and ferrimagnets. These calculations also enable us to understand the thermodynamic properties at low temperature. This work is nearly finished.

Publications:

Harris, A. B., "Nature of the 'Griffiths' Singularity in Dilute Magnets", Phys. Rev. (Accepted)

Harris, A. B., "Upper Bounds for the Transition Temperatures of Generalized Ising Models", J. Phys. C 1, 3082 (1974)

Harris, A. B. and Lubensky, T. C., "Renormalization-Group Approach to the Critical Behavior of Random-Spin Models", Phys. Rev. Lett. 33, 1540 (1974)

Holcomb, W. and Harris, A. B., "Spin Waves in Dilute Antiferromagnets", A. I. P. Conf. Proc. (Magnetism Conference, 1974) (Accepted)

Kirkpatrick, S. and Harris, A. B., "Static Properties of Dilute Ferri- and Antiferromagnets", A. I. P. Conf. Proc. (Magnetism Conference, 1974) (Accepted)

Lubensky, T. C. and Harris, A. B., "Critical Properties of Random Spin Systems Using the Renormalization Group", A. I. P. Conf. Proc. (1974 Magnetism Conference) (Accepted)

9. Electronic Phenomena in Normal and Superconductors

D. N. Langenberg, Professor of Physics

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Support: NSF-MRL
ARPA-LRSM
NSF
ONR
AROD

Objective and Approach: The principal objective of this program is an understanding of two related classes of phenomena in superconductors:
(1) Josephson effects in systems of weakly coupled superconductors.
(2) Dynamic behavior of superconductors strongly perturbed from equilibrium.

The Josephson effects are of both fundamental and practical interest, the latter because they provide the basis for a growing number of cryoelectronic devices with unique capabilities. We are investigating some basic features of Josephson phenomena as well as their potential application to the detection and generation of very high frequency radiation.

Nonequilibrium phenomena are important in current-carrying superconductors, including especially certain types of Josephson devices, and in superconducting devices used for generation and detection of phonons at frequencies approaching 10^{12} Hz. A practical phonon spectroscopy in this important frequency range is emerging from recent developments in this field.

Progress: We have completed a study of magnetoplasma effects in PbTe which has yielded a complete and consistent picture of the anomalous lattice dielectric behavior of this semiconductor. It is paraelectric, having a large ($\sim$ 3500 at 4.2 K) and strongly temperature dependent dielectric constant. Our results resolve most of the discrepancies among a large number of previous studies of the lattice dielectric constant of this material, which gave numbers ranging over more than an order of magnitude. In the course of this work, we have also obtained improved values of several of the principal effective mass parameters and shown how they can be fitted into an improved band structure model.

In a study of the properties of very small Josephson tunnel junctions, we have developed a simple and inexpensive technique for fabrication of superconducting microbridges and very small tunnel junctions. With these small junctions, and with junctions made with film thicknesses as low as 500 Å, we have improved by two orders of magnitude the coupling between the junction and external rf fields. This improvement allows the possible use of Josephson tunnel junctions in microwave generation and detection systems. We are continuing investigation of an anomalous temperature dependence of the critical current which we have observed in these small tunnel junctions.

We are continuing studies of nonequilibrium superconducting states induced by laser irradiation, using measurements of microwave reflectivity to probe modifications of the quasiparticle distribution in superconducting films caused by very short pulses of light. We have extended these experiments to "one-dimensional" superconductors, i.e., micron sized filaments. The objective here is the creation of photon-induced superconducting weak links which will exhibit the Josephson effects. We have been able to induce dc weak link characteristics like those observed in more conventional systems of weakly-coupled superconductors, and have preliminary evidence for the existence of the ac Josephson effect in our photon-induced weak links. In related experiments we have observed substantial changes in the behavior of superconducting microbridges in which quasiparticles are extracted or injected through a normal-conductor counter-electrode. Studies of the behavior of this three-terminal "superconducting transistor" device are continuing.

We are in the course of a theoretical calculation of the intrinsic quasiparticle recombination time, the quasiparticle thermalization time, and the phonon pair-breaking time for a variety of superconductors, using the Eliashberg equations and experimental information on the electron-phonon coupling function. We are also attempting to calculate the quasiparticle and phonon energy distributions in a non-equilibrium superconductor. The hope is that these results will provide for the first time a realistic quantitative theoretical picture of a nonequilibrium superconductor for comparison with our experimental results.

Publications:

Buckner, S. A. and Langenberg, D. N., "Temperature Dependence of the Riedel Singularity", Low Temperature Physics-LT 13, Vol. III, p. 285, Eds., K. D. Timmerhaus, W. J. O'Sullivan and E. F. Hammel, Plenum Press, New York (1974)

Chen, J. T. and Langenberg, D. N., "Fine Structure in the Anomalous DC Current Singularities of a Josephson Tunnel Junction", Low Temperature Physics-LT 13, Vol. III, p. 289, Eds., K. D. Timmerhaus, W. J. O'Sullivan, and E. F. Hammel, Plenum Press, New York (1974)

Dahm, A. J. and Langenberg, D. N., "Blackbody Radiation from a Single Mode Source: A Demonstration", Am. J. Phys. (Accepted)

Dahm, A. J. and Langenberg, D. N., "Comments on the Josephson Plasma Resonance in ^{3}He(A)", Part IV, Proc. Sanibel Symposia

Dahm, A. J. and Langenberg, D. N., "Nonlinear Effects in the Josephson Plasma Resonance", J. Low Temp. Phys. 19, 145 (1975)

Langenberg, D. N., "Characteristic Times in Superconductors", in Festkörperprobleme-Advances in Solid State Physics, Vol. XIV, p. 67, Ed., H. J. Queisser, F. Vieweg & Sohn, Braunschweig (1974)

Pedersen, N. F., Finnegan, T. F. and Langenberg, D. N., "Evidence for the Existence of the Josephson Quasiparticle-Pair Interference Current", Low Temperature Physics-LT 13, Vol. III, p. 268, Eds., K. D. Timmerhaus, W. J. O'Sullivan and E. F. Hammel, Plenum Press, New York (1974)

Rothwarf, A., Sai-Halasz, G. A. and Langenberg, D. N., "Quasiparticle Lifetimes and Microwave Response in Nonequilibrium Superconductors", Phys. Rev. 33, 212 (1974)

Sai-Halasz, G. A., Chi, C. C., Denenstein, A. and Langenberg, D. N., "Effects of Dynamic External Pair Breaking in Superconducting Films", Phys. Rev. 33, 215 (1974)

Tyler, I. L., Denenstein, A. and Langenberg, D. N., "Infinite-Hold-Time Electronic Ramp Generator", Rev. Sci. Instr. 45, 1007 (1974)

Yeh, J. T. C., "Technique for Fabrication of Superconducting Microbridges and Small Josephson Tunnel Junctions", J. Appl. Phys. 45, 4617 (1974)

Yeh, J. T. C. and Langenberg, D. N., "Observations on Small Tunnel Junctions: Anomalous Critical-Current Temperature Dependence, Periodic Structure, and Microwave Detection", Proc. 1974 Applied Superconductivity Conference, IEEE Trans. Mag., MAG-11, 683 (1975)

10. Theoretical Studies of Critical Phenomena

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Research Assistant: J-h. Chen

Support: NSF-MRL
NSF
ONR

Objective and Approach: The objective of this work is to understand the nature of and to calculate critical exponents for second order phase transitions in a variety of different materials. The materials investigated in the past year include liquid crystals, semi-infinite magnets and randomly diluted magnets. The techniques employed include the renormalization group and static and dynamic mean field theory.

Progress: Much of the work in the past year has involved various liquid crystalline phases. Liquid crystals are composed of long organic molecules. In the nematic phase, these molecules diffuse freely but are oriented with their long axes along a common direction. The cholesteric phase is similar to the nematic phase but with the direction of molecular orientation twisted in a helical pattern. The smectic-A phase consists of parallel planes. The molecules reoriented perpendicular to these planes and are free to diffuse within a given plane but not from plane to plane. The smectic-C phase is the same as the smectic-A phase but with the molecules tilted at an angle to the normal to the planes.

In the past year, I have shown that the cholesteric to smectic-A transition is analogous to the superconducting transition in the presence of an external magnetic field and estimated the latent heat of this transition.

Bob Meyer (of Harvard University) and I completed our investigation of the generalized mean field treatment of the nematic to smectic-A transition. This work includes an investigation of the effects of polar molecules and asymmetric center of mass distribution on the transition. This study leads to a qualitative characterization of molecules that are expected to exhibit second order transitions to the smectic-A state. This work is currently being prepared for publication.

My graduate student Jing-huei Chen and I have made considerable progress in understanding the nematic to smectic-C transition. We have introduced a model free energy that yields a second order nematic to smectic-C transition in mean field theory. Using this model, we have calculated the Frank elastic constants and the twist viscosity using mean field theory. All diverge as the correlation length squared near the transition.

Marco de Moura, a postdoctoral from Brazil and I have studied the ferromagnetic and the smectic-A to smectic-C phase transitions in an anisotropic compressible lattice. We find that the ferromagnetic transitions are unstable with respect to lattice distortions whereas the smectic-A to C transition is not.

A. Brooks Harris and I have successfully applied the renormalization group to the calculation of critical exponents for phase transitions in randomly diluted magnets

Morton H. Rubin and I continued our studies of critical phenomena in semi-infinite systems. We treated lattices with enhanced exchange on the surface using mean field theory and the renormalization group.

Publications:

Halperin, B. I. and Lubensky, T. C., "On the Analogy between Smectic-A Liquid Crystals and Superconductors", Solid State Commun. 14, 997 (1974)

Harris, A. B. and Lubensky, T. C., "Renormalization-Group Approach to the Critical Behavior of Random-Spin Models", Phys. Rev. Lett. 33, 1540 (1974)

Lubensky, T. C., "Critical Properties of Random-Spin Models from the ϵ-Expansion", Phys. Rev. B 11, 3573 (1975)

Lubensky, T. C., "Latent Heat of the Cholesteric to Smectic-A Transition", J. Physique (Paris) (Accepted)

Lubensky, T. C. and Harris, A. B., "Effect of Randomness on Critical Behavior of Spin Models", Proc. of the 1974 MMM Conf. (Accepted)

Lubensky, T. C. and Rubin, M. H., "Critical Phenomena in Semi-Infinite Systems I: ϵ-Expansion for Positive Extrapolation Length", Phys. Rev. B 11, 4533 (1975)

Lubensky, T. C. and Rubin, M. H., "Critical Phenomena in Semi-Infinite Systems II: Mean Field Theory", Phys. Rev. (Accepted)

11. Spectroscopic and Chemical Properties of Small Aggregates of Binary Compounds and Metals

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Postdoctoral Fellow: C-K. Chi

Research Assistant: R. Teichman, III

Support: NSF-MRL
ARPA-LRSM

Objective and Approach: This research deals with some selected types of materials which have potential utility as conductors, semiconductors or catalytic agents. The species are prepared and preserved by trapping them in a solid inert gas matrix at low temperatures. The materials of immediate interest are the Group IV - Group VI compounds, the SN compounds and several metals.

The objective is to characterize these materials by various spectroscopic techniques as a function of the state of aggregation from the diatomic molecule (MX or M_2) to larger aggregates or polymers ($(MX)_n$ or M_n) and thereby contribute to the understanding of the formation of polymers. Once this is accomplished, we plan to cause these aggregates to react with small molecules and to study the changes in the states of the aggregates and of the molecule introduced with the objective of contributing to the understanding of reactions at surfaces.

Progress: The matrix isolation technique is a valuable method for studying molecular species which would otherwise be difficult to prepare and preserve. The role of the matrix itself in the spectroscopic properties of the types of systems under study in this research has hitherto not been very well understood. This past year we have been able to shed much light on this problem. The structure of a vibronic emission or absorption band of a matrix-isolated molecule depends upon the degree of coupling between the states of the guest molecule and the phonon states of the host matrix. If the coupling is strong, most of the band intensity is located in relatively broad multiphonon sidebands; if the coupling is weak the intense feature of the band is the very sharp zero-phonon line. We have studied systems in which both extremes of coupling are exhibited. In the weak coupling cases with sharp lines we have been able to resolve much isotopic structure in the spectra (15 isotopic species of PbSe). Moreover we have been successful in producing absorption of light with consequent excitation and emission by a single isotopic species. This demonstrates the possibility of using the matrix method for isotopic separation.

By irradiating our matrix-isolated molecules with laser lines in the visible, we have been able by biphotonic processes to excite rather efficiently emission of light well into the ultraviolet.

We have observed and characterized a host of hitherto unknown electronic states of the IV-VI diatomic and tetratomic molecules.

Some preliminary experiments of reacting molecules, like O_2, with small aggregates of IV-VI compounds and of a few metals have been carried out but the results have not been analyzed.

Resonance Raman studies of several alkali metal TCNQ salts in the solid form and of the $TCNQ^-$ ion in solution have been completed. The results allow us to identify many of the vibrational modes of the ion and by comparison with the parent TCNQ molecule to draw qualitative conclusions regarding the electronic structures of the molecule and ion.

In the $(SN)_x$ problem, we have thus far examined the infrared, Raman and visible - uv spectra of S_2N_2 and S_4N_4 both as solid films and also isolated in solid matrices. We have also observed the polarized Raman spectrum of crystalline S_4N_4. Matrix isolation studies of the volatilization of the SN polymer leads us to conclude that the products are S_2N_2, S_4N_4 and a third as yet unidentified molecule. We have also observed the polymerization of these products when the matrix is irradiated with blue laser light.

Publications:

Chi, C-K. and Nixon, E. R., "Resonance Raman Studies of RbTCNQ and KTCNQ", Spectrochimica Acta (Accepted)

Teichman, R. A. and Nixon, E. R., "The A → X Emission Spectra of PbS and PbSe in Neon Matrices: Enhanced Emission from Isotopes and Matrix Sites", J. Mol. Spectry. 57, 14 (1975)

Teichman, R. A. and Nixon, E. R., "Biphotonic Stimulation of Emission and Matrix Effects in Lead Sulfide in Solid Argon", J. Mol. Spectry. 55, 192 (1975)

Teichman, R. A. and Nixon, E. R., "Vibronic Spectra of Matrix-Isolated Lead Sulfide", J. Mol. Spectry. 54, 78 (1975)

12. Theoretical Investigation of Electronic Properties of IV-VI Compounds and Alloys

S. Rabii, Associate Professor of Electrical Engineering and Science

Research Assistant: S. W. W. Liu

Support: ARPA-LRSM

Objective and Approach: The IV-VI compounds and their alloys are a family of important technological materials in view of their present application as sources and detectors for infrared radiation and their potential use as chemical sensors. The objective of this work is to use theoretical techniques to obtain an accurate and coherent picture of their electronic structure. This basic information is then employed to study their electrical, optical, and elastic properties and their interrelationship. It will have the following parts:

1. Investigation of the electronic structure of the lesser studied members of this family (GeS, SnS, PbPo). On one hand we hope to show potential applications for these members, and on the other hand we will use the trend in their calculated properties to clear some yet unanswered questions about these materials.

2. We will continue to develop our formalisms for the study of pseudobinary alloys so that they will be able to handle nonisoelectronic alloys ($Pb_{1-x}Cd_xS$) and alloys with structural phase change as a function of composition ($Pb_{1-x}Sn_xS$).

3. Study of the electronic structure of isolated clusters of PbS both with and without defects. The results will not only help us in understanding the role of defects in the electrical, optical, and elastic properties of these materials, but will also furnish information that can be directly compared with optical spectra of aggregates of IV-VI compounds measured by E. Nixon.

Progress: Work on the electronic structure of semiconducting alloys culminated in the development of a formalism based on an expansion of the coherent potential approximation (CPA). The formalism was used to obtain the first and only rigorously-based calculation of the electronic structure of $Pb_{1-x}Sn_xTe$ with very successful results.

Our calculations of the basic energy band structure of the high pressure phase (NaCl structure) of CdS has concluded and the results indicate an indirect band gap semiconductor with a gap of 1.5 eV. There is also a second gap appearing in the conduction band. These calculations have taken on added importance since recently two epitaxial thin films of CdS grown on CaF_2 substrate in our laboratory have been shown to have NaCl structure and a lattice constant near that used for the calculation. This work will

furnish considerable basis for the interpretation of the experiments to be done on these films.

Our preliminary calculations of the relativistic band structure of PbPo have indicated that this compound is a semimetal due to increased relativistic effect in Po. Furthermore the results have answered the long standing puzzle of the anomaly in the band gap sequence of PbS, PbSe and PbTe and have shown that PbTe is the unusual member of the family. This anomaly is due to a similar anomaly in the size of the Te atom.

Publications:

"Physics of IV-VI Compounds and Alloys", Ed., S. Rabii, Gordon and Breach, March 1975

Rabii, S., "Effect of Strain on the Secondary Band Extrema of PbS, PbSe, PbTe, and SnTe", Phys. Rev. B7, 3830 (1973)

Rabii, S. and Lasseter, R. H., "Band Structure of PbPo and Trends in the Pb Chalcogenides", Phys. Rev. Lett. 33, 703 (1974)

Sood, A. K., Yang, C. Y. and Fischer, J. E., "Effect of Chlorine Exposure on the Thermoreflectance Spectra of Lead Chalcogenide Films", Thin Solid Films 23, 337 (1974)

13. Interface Studies on Electronic Materials

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H. J. Gray, Jr., Professor of Electrical Engineering and Science
J. E. Fischer, Associate Professor of Electrical Engineering and Science

Research Assistants: S. Aymeloglu
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Support: NSF-MRL
ARPA-LRSM
MOS Technology
PSEF
NSF
BTL
U of P

Objective and Approach: Semiconductor devices involve thin films in intimate contact with the active, semiconductor region. Our studies deal with the materials problems that exist in silicon itself, silicon-silicon dioxide interfaces, two dimensional electron gases at the Si-SiO_2 interface and, finally, the effect of gases on thin layers of silicon, and heterojunctions involving silicon. Why is silicon so ubiquitous in our studies? The reason is that silicon technology is so highly developed that anything that adds to its broader application, can be readily put into practice.

Silicon is unquestionably the best understood material known. However, the production of silicon wafers varies sufficiently that various defects can arise that influence yield and reliability in final devices. We are developing a number of measurement methods which reveal inhomogeneities of various types, e.g., the density and approximate profile of ion implanted species; surface flaws such as scratches, micro-cracks and polish induced dislocation patterns; deep impurities, etc.

The silicon-silicon dioxide interface is where the action is on all MOS type digital and linear integrated circuits. In the layman's language, the reliability and reproducibility of this interface is why you can have an SR-50 or an H-P45 hand calculator so cheap. We are examining details of the Si-SiO_2 interface such as how two dimensional electron behavior at the interface is dependent on various types of scattering processes; how the oxygen content in the silicon affects the transport properties at the interface; the role of vacancies in the Si or the SiO_2 on surface state behavior; surface potential variations due to oxide changes and bulk doping fluctuations.

The heterojunction and gas effect studies are closely related to each other. The heterojunction layer is quite thin in our work and can be influenced by either a surface adsorption of a given species or in-diffusion of the species. In addition, the particular example of the PbS-Si heterojunction is noteworthy since it has sufficient sensitivity to infra-red radiation that it could be used to make infra-red vidicons with additional development. We have shown that thin PbS-Si heterojunctions are useful atomic hydrogen sensors and demonstrate the general principle that heterodiodes can make good chemical detectors. The basic reason is that in a heterodiode, the back bias current is a function of the doping and consequently, the fermi level of the thin layer. If the in-diffusing species affects the fermi level, it will change the back bias current. The sensitivity appears to be quite respectable.

The silicon base for this program is an initial stage prior to undertaking other studies on III-IV materials. We plan to leave this part for a later time.

Progress: Progress in this work overlaps several of the areas mentioned above. The most active areas have dealt with the PbS-Si heterojunction and its sensitivity to gas effects and the development of non-destructive material evaluation methods for silicon processing/devices. We believe that we have shown for the first time how a heterodiode can be used as a chemical sensor. This leads to the general characterization of a new class of chemical sensor elements and raises the opportunity of a deeper understanding of many different single crystal and polycrystalline sensors. Briefly put, if the depletion region of one side of a heterojunction diode is greater than the thickness of the layer, then any electrically active impurity that diffuses into that layer changes the barrier height of the heterodiode. As a result, the back bias current will be a sensitive measure of the concentration of the electrically active impurity. In some of the new transition metal oxide oxygen sensors, grain boundary effects may not be the only cause of barrier height variations. Bulk oxygen vacancy destruction may lead to fermi level variations in the microcrystallites that are just as significant as those in the grains. This is very similar to the H effect in polycrystalline PbS-Si heterodiodes. In a review paper published by one of us (J. N. Zemel) in February of this year, the use of a Pd layer to detect H_2 was discussed. At the same time a paper appeared in APL describing a MOSFET with a Pd gate which serves as a detector. Combined Pd-PbS or PbSe-Si heterostructure would make an attractive system for detecting the relative concentrations of H and H_2 in a system. Such a combination might prove valuable in the study of hydrocarbon cracking.

The work on silicon and silicon based devices addressed a simple question; what phenomena influence yield? Process technology in IC fabrication has reached a stage where additional knowledge of the materials is essential. During the year we developed two new techniques for the study of silicon. One is quite old in fact but the particular form of the measurements makes it possible to examine slices of silicon semi or completely

automatically. The second permits the device manufacturer to probe the bulk properties of a completed device with considerable precision.

The surface photovoltage (SPV) is an old tool, dating back over 20 years for the study of semiconductor surface properties. It is a change in the contact potential with light measured between the semiconductor and a semitransparent metal electrode. A well focused laser beam, 50 μ in diameter, scans across the surface of a silicon slice and the SPV is recorded. The variation from point to point is characteristic of a combination of effects including surface and bulk recombination processes and the amount of band bending. Systematic differences were observed on slices from different manufacturers that suggest rather large bulk rather than surface potential fluctuations. The magnitude of the SPV also varied systematically from manufacturer to manufacturer. Finally, yield data indicates a correlation with manufacturer despite the fact that the slices all meet the same electrical property specifications. A joint program with MOS Technology is now examining the yield of a group of measured slices to see if more detailed correlations can be obtained. Any information leading to yield improvement would have a dramatic and profound impact on corporate profits in the U. S. semiconductor industry. The depressed state of the semiconductor industry influences the job opportunity for our graduates and any improvement here would greatly help our future.

The behavior of a MOSFET structure in the freezeout regime provides valuable insight into both bulk and surface properties. As freezeout proceeds, the Debye length gradually increases. The depletion region also increases rapidly. Any variations in $N_A^- - N_D^+$ will tend to influence the freezeout temperature quite strongly. We have shown that simple MOSFET's will fit the usual picture quite nicely. The capacitance (C) and imaginary part of the capacitance (the parallel conductance G_p) as a function of gate voltage (Vg) is commonly used to characterize the Si-SiO_2 interface. When freezeout is occurring on the accumulation side of the C-Vg curve, the acceptor levels behave like deep traps and the dielectric relation time begins to dominate the capacity. The detailed study of the temperature dependence of C indicates good agreement with simple theory. However, the deviations suggest a fluctuation in $N_A^- - N_D^+$ similar to that observed in the SPV. Furthermore, C(T) and G_p(T) provide very useful information on ion-implant profiles, doping of silicon gates and, interestingly, the effect of magnetic fields on the silicon. The latter can be used to observe Zeeman and Landau level splittings with field. Further studies are greatly needed.

Publications:

Aymeloglu, S. and Zemel, J. N., "Freeze-Out Effects on N-Channel MOSFET's", Second Annual Conf. of the Physics of Compound Semiconductor Interfaces

Duh, K. Y. and Zemel, J. N., "Properties of PbS Epitaxial Films Grown by a Hot Wall Method", Thin Solid Films 26, 165 (1975)

Lopez, A., Duh, D. and Zemel, J. N., "Deep Impurity Levels in Epitaxial PbS Films", Mater. Sci and Eng. 17, 63 (1975)

Young, J. J. and Zemel, J. N., "Kinetics of the Hydrogen Effect on PbSe Epitaxial Films", Thin Solid Films (Accepted)

Zemel, J. N., "Gas Effects on IV-VI Semiconductor Films", Surface Physics of Phosphors and Semiconductors, Academic Press, London (Accepted)

Zemel, J. N., "Ion-Sensitive Field Effect Transistors and Related Devices". Anal. Chem. 47, 255A (1975)

Zemel, J. N., Rahnamai, H. and Young, J. J., "Gas Effects on Lead Chalcogenides", CRC Reviews (Accepted)

F. BIOMATERIALS

1. Piezoelectric Properties of Bone

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M. E. Steinberg, Associate Professor of Orthopaedic Surgery

Postdoctoral Fellows: J. K. Koh
R. T. Lefkoe

Support: NSF

Objective and Approach: Although the "piezoelectric" effect in bone was reported in 1954, to this date there has not been a rigorous characterization of the effect and, therefore, little or no progress made in understanding either the origin of the effect or its physiological significance. It is an extremely complex problem for several reasons: a) bone is a multicomponent, multiphase composite system; b) bone is viscoelastic and its viscoelastic properties (for live bone) are not well characterized; c) models for visco-elastic-piezoelectric systems are only now beginning to be considered.

This project has the following specific objectives: 1) Characterize the internal "piezoelectric" effect in bone as a function of stress, strain and rate of deformation under physiologic ambient conditions. 2) Determine the origin of the effect within the multicomponent, composite structure of bone. 3) Determine the mechanism of macroscopic electrical signal generation in bone and determine its physiological role in bone growth, remodeling and repair. The approach that is being used is: 1) Use a special load frame and environmental test chamber for controlled deformation-piezoelectric voltage measurement. 2) Simultaneous measurements of viscoelastic properties in compression and tension along with voltage measurements on moist recently excised human cortical bone. 3) Four point bending measurements are being done since both compression and tension take place, and development of macroscopic voltages can be studied. That is, given the relationship among stress, strain, and rate for both compression and tension, the four point bending mode is completely characterized. Knowing the voltage contribution in compression and tension enables a comparison with actual voltage determination in this mode. 4) All test data will be augmented by structure, morphology, and composition studies of all samples measured.

Progress: Experiments on whole rat femurs indicate that the electrical signal per percent strain generated during four point bending increases with the age of the rat up to 13 weeks and remains constant thereafter. The flexure modulus also increases during the same period of time. Formalin

fixation also increases the electrical signal per percent strain although the modulus is unaffected. Injection of BAPN prior to sacrifice decreases the electrical signal and the modulus as does boiling in saline. All of the above experiments confirm the role collagen plays in generating the electrical signal.

The electrical signal generated in whole rat femurs from rats 13 weeks and older agrees with values obtained in machined samples of one year old bovine bone, namely $6^{mV}/\%G$. Analysis of bone morphology further indicates that the conventional matrix representation must be modified to account for "random" osteonal configurations.

V. THE CENTRAL RESEARCH FACILITIES

Of central importance to the LRSM program in the materials sciences is the operation and maintenance of the central research facilities. Each has a faculty advisor, and all but three have full-time professional laboratory supervisors. Five of the facilities have additional permanent staff.

The general philosophy of operation is that the supervisors are not to provide service on demand. They are to maintain the equipment and give instruction in its use, so that the students, post-doctoral fellows, and sometimes even the faculty can carry out the necessary operations. Although there are a few exceptions to this procedure, notably in the provision of slides and other photographic services and in the calibration and repair of electronic gear, generally the system operates as described.

It is difficult to overestimate the importance of these facilities for the LRSM research program. Almost all of the experimental work is directly dependent upon one or more of them, and to provide and maintain equipment and personnel on the scale required would be virtually impossible under a system of individual grants and contracts.

Mechanical Testing

Faculty Advisor: Prof. Charles J. McMahon, Jr.
Laboratory Supervisor: R. de la Veaux

This facility has now been consolidated in one area, and includes facilities for fatigue, creep, and general mechanical testing. The policy in setting up the facility has been to obtain the most versatile and flexible machinery, and to equip it with a wide range of accessories to permit easy interchange of function. Thus, the fatigue laboratory contains two channels of closed-loop electrohydraulic testing equipment usable on seven load frames ranging in capacity from 250 lbs. to 50,000 lbs. One frame is equipped with a high temperature, high vacuum chamber, for both resistance and induction heating to 1450°C. An analog computer can be used in the command mode in either channel. Recording equipment comprises x-y recorders, oscilloscopes, Brush recorders, and a punched tape/teleprinter system. A digital computer has been installed to carry out the functions of command, closing the loop and acquiring data, all with improved speed and accuracy. Virtually any kind of mechanical test can be carried out from fracture mechanics to fatigue at 200 Hz. The creep laboratory has two Satec systems with instrumentation, vacuum systems and furnaces which permit complex creep and stress relaxation work up to 6,000 lbs. and 2200°F. A punched tape/teleprinter system has been added for data reduction. The general laboratory contains three Instron machines with a complete range of accessories, including high and low temperature equipment.

This facility is central to the scope and excellence of our present research effort in materials failure. It provides the equipment for all aspects of the program: cyclic-stress strain, creep-rupture, embrittlement, fatigue fracture, high temperature deformation of metal alloys, and deformation studies of polymers and amorphous alloys.

Organic Materials Preparation-Analytical Chemistry

Faculty Advisor: Prof. Robin M. Hochstrasser
Laboratory Supervisor: Dr. A. R. McGhie
Deputy Supervisor: M. R. Kresz

Most aspects of inorganic analysis, with particular emphasis on trace level determinations, are provided by this facility, including atomic absorption, emission spectroscopy, gas chromatography, ultraviolet and visible absorption spectroscopy, scintillation and geiger counting, and a variety of electroanalytical techniques.

For organic materials analyses we have, in addition to those listed above, analytical high pressure liquid chromatography and thin layer chromatography. Approximately 60% of the analytical work load involves routine measurements for characterizing reagent purity and contamination levels in starting materials and for establishing the composition of in-process and finished specimens. The remaining 40% of the effort is devoted to devising new procedures for solving specific analytical problems.

The facility's principal functions in organic materials preparation are separation/purification, and the growth of pure and doped single crystals. Equipment and techniques available include distillation, sublimation, preparative gas chromatography, thin layer and high pressure liquid chromatography, zone refining and crystal growth from the melt, vapor and solution.

A major part of the effort in organic materials preparation is in devising methods for producing the ultrapure materials required for the studies of the optical, electrical and magnetic properties of organic crystals and charge transfer compounds being conducted by our research group in the molecular crystals area.

Surfaces

Faculty Advisor: Prof. E. Ward Plummer
Laboratory Supervisor: Dr. H. C. Feng

At present this facility has a general purpose Auger spectrometer equipped with ion sputtering, electron beam heating and fracture equipment. The Auger spectrometer is used for a wide variety of experiments where

the chemical composition as well as a depth profile of a surface is desired. The Auger capability has been supplemented with the purchase of a new Scanning Auger Spectrometer to be used primarily in connection with the studies on embrittlement of steel. This major item of equipment (~ $100K) was bought with half support from the MRL and the other half from external funding.

The following experimental capabilities are available as support for the surfaces and interface program:

(1) Field emission energy analyzer system with field ion capabilities.
(2) UV photoemission system, both large solid angle collection for dynamic reaction studies and angular resolved for surface conformational studies.

The following components are available for any experiment:
(1) Low energy electron diffraction, with rotatable Faraday cup for individual current-voltage profiles.
(2) Mass spectrometry for chemical decomposition studies.
(3) High ion current sputtering capabilities.
(4) CMA Auger spectrometer.

All of these facilities are designed in a modular fashion so that components may be shifted from one experiment to another.

X-Ray Diffraction

Faculty Advisor: Prof. Jerry Donohue
Laboratory Supervisor: H. Katz

The X-ray diffraction facility is equipped for crystal and molecular structure determinations using single crystal and powder techniques, identification of materials, crystal orientation and perfection measurements, elemental analysis by fluorescence, small angle scattering and temperature dependent phase change studies. The major equipment in the facility includes a Picker four-circle single-crystal diffractometer with a PDP-8 computer control unit; a Philips and a General Electric diffractometer, each with lithium fluoride monochromator; a vacuum fluorescence unit; a single crystal orienter; a scanning digital microdensitometer; a high temperature diffractometer attachment, a small angle scattering unit; a rotating anode x-ray unit in a cold room; and a variety of cameras for single crystal, powder and back reflection measurements.

Because all research groups in the program are concerned with the relationship between the structure of a material and its properties, the facility is involved in a wide variety of research problems. Prominent among these are complete x-ray crystal structure determinations of both

organic and inorganic crystals of interest to the molecular crystals, electronic and magnetic materials, and biomaterials groups. Researchers in the area of materials failure use the x-ray facility for studies of the temperature dependence of long range order in alloys and of the topography of alloy surfaces as related to mechanical properties. Measurements of crystal orientation for optical and magnetic measurements and examination of thin films for crystal perfection are carried out routinely.

Spectroscopy

Faculty Advisor: Prof. Eugene R. Nixon

This facility has equipment for optical measurements from the vacuum ultraviolet to the far infrared. Prism, grating and interferometric spectrometers are available for emission, absorption, reflection, laser Raman and Brillouin scattering studies. In addition to applications in materials identification and analysis by researchers in the chemical metallurgy area, the facility is involved in major research projects on optical phenomena in organic crystals, charge-transfer compounds, and semiconductor materials, and on a range of problems related to thin films and surface properties. The equipment is used principally by a relatively small group of students and postdoctoral fellows, and no laboratory supervisor is employed.

Electron Microscopy-Metallography-Photography

Faculty Advisor: Prof. Campbell Laird
Laboratory Supervisor: R. G. White
Laboratory Assistants: A. M. Lindemanis
A. Vaskelis

The major equipment in this facility includes a Siemens Elmskop I and a Philips EM300 transmission electron microscope, a Philips AMR Mark III electron microprobe, and a JEOL JSM U3 scanning electron microscope equipped with an EDAX energy dispersive x-ray spectrometer of better than 200 eV resolution. The Philips EM300 and the JEOL JSM-U3 with the EDAX x-ray spectrometer are equipped so that images and x-ray data can be stored on a centrally located video tape deck. Ancillary equipment includes an ion micromilling instrument, vacuum evaporator, ultra-microtome, laser facility, and optical microscopes. The major use of the facility has been on research projects in materials failure, chemical metallurgy, electronic materials, organic and inorganic conductors, and biomaterials. In the past year over 95 different researchers amassed a total of nearly 2000 hours of equipment use time. This is our most widely used facility.

The metallography section of this facility provides services for materials failure studies. It includes equipment for specimen sectioning, mounting, grinding, lapping and polishing, and metallographic microscopes

equipped for photomicrography. Several hardness and microhardness testers are also located in the center.

The photography section contains equipment for film and print processing and enlarging for photomicrographs and other forms of data recorded photographically. There are also provisions for slide-making.

Magnetic Field

Faculty Advisor: Prof. Charles D. Graham, Jr.
Laboratory Supervisor: P. J. Flanders
Laboratory Assistant: L. Cheskis

The High-Field Magnet Laboratory comprises a 6 megawatt motor-generator set, a heat exchange system capable of dissipating 4 megawatts continuously, and 4 Bitter-type water-cooled solenoids ranging from a 1-inch bore, 135 kOe to a 5-inch, 60 kOe magnet with radial access ports. Two magnet stations permit preparation for new experiments to proceed simultaneously with magnet operation. The Laboratory also operates six electromagnets, ranging in size from 12-inch to 2-inch pole diameter and equipped with a variety of magnetic measuring equipment. The magnet facility is one of four comparable installations in the United States.

The facility is used mainly in connection with the programs on electronic and magnetic materials and on molecular crystals. This facility has not received the broad use anticipated partly because of the research interests of the LRSM faculty and partly because of the success and current availability of superconducting magnets. As a result, the LRSM Policy Committee has decided to reduce LRSM support for the facility by approximately a factor of two. The principal users will supply the additional funds to maintain the facility for their use via external contracts and grants.

Instrumentation

Faculty Advisor: Prof. John E. Fischer
Laboratory Supervisor: S. Macri
Laboratory Assistant: F. Hellmig, Jr.

This laboratory performs a number of inter-related and specialized functions: (1) standardization and calibration of all types of electronic equipment and laboratory apparatus; (2) design of specialized instrumentation; (3) maintenance and repair of laboratory equipment; and (4) providing a pool of general purpose instruments for short term use by members of the LRSM.

The electrical standards lab is equipped for a number of precision calibrating services, all traceable to the National Bureau of Standards. The laboratory has also transportable equipment to compare laboratory standards with NBS.

Materials Processing

Faculty Advisor: Prof. David P. Pope
Laboratory Supervisor: W. J. Romanow
Laboratory Assistants: G. Wood
L. Cheskis

The Materials Processing Facility is comprised of five integrated laboratories; thin film deposition, melting, mechanical working, heat treating and materials preparation. Its function is to supply high quality materials for experimental study throughout the program.

The thin film deposition laboratory has facilities for making thin films of either single or co-evaporated materials by resistance heated sources or by evaporation with a Varian 2 kw e-gun. Substrate heating, cooling or pre-evaporation cleaning (by glow discharge) are available. The melting laboratory has facilities for both single crystal growing and vacuum induction melting. There is equipment for growing crystals by a number of different techniques. The mechanical working laboratory has facilities which include rolling mills, rotary swagers, and wire-drawing dies. The heat treating laboratory has equipment and facilities for the thermal treatment of materials over a wide range of temperatures and atmospheres. Included are tube furnaces, salt pot furnaces, air furnaces, muffle furnace and atmosphere furnaces with inert, oxidizing, reducing or evacuated ambients. Two Brew high temperature high vacuum furnaces are available for temperatures up to 3000°C. The materials preparation laboratory has provisions for powder preparation, particle sizing, materials handling and crystal cutting.

This is probably the busiest and most widely used of all the central facilities. In addition to a wide range of metals and alloys, samples of oxides, halides, sulfides, and other compounds are prepared for work in all of the thrust areas except molecular crystals.

Mass Spectrometry

Faculty Advisor: Prof. John G. Miller

A CEC 21-130 Mass Spectrometer is maintained by LRSM in the Chemistry Building, where the Chemistry Department provides an operator. The instrument has been modified to increase the mass range, and has been equipped with a peak-height ratio module and a recorder for determining isotope compositions. It provides a useful service at very small cost. The completion of the new Chemistry Building has permitted the machine to be installed in a room devoted only to mass spectroscopy, and a new and better qualified operator has been employed. The LRSM support required is minimal; less than $1000 per year. Additional Mass Spectrometry equipment is available in Prof. Cava's lab and is routinely used in the organic synthetic work.

Data Processing Center

Faculty Advisor: Prof. Donald H. Voet

This facility consists of a PDP8/I computer with 8K-word memory, 32K-word magnetic disk storage, high-speed paper tape reader and punch, and teletype input-output, plus keypunches and an electronic desk calculator. It was established to accommodate the variety of small to medium computing problems generated throughout our materials science program. A large number of students and faculty employ the facility regularly for data reduction, curve fitting, program debugging, and similar jobs. The equipment is also used for the transfer of data from punched tape to punched cards for use on the University IBM 370 facility. A scanning microdensitometer, connected on-line to the PDP8/I computer, is used for analyzing x-ray diffraction data recorded on photographic films.

VI. LRSM ACADEMIC STAFF

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Burstein, Elias, Professor of Physics

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Donohue, Jerry, Rhodes-Thompson Professor of Chemistry

Egami, Takeshi, Assistant Professor of Metallurgy and Materials Science

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Garito, Anthony F., Associate Professor of Physics

Gaskell, David R., Associate Professor of Metallurgy and Materials Science

Girifalco, Louis A., Professor of Metallurgy and Materials Science and Associate Dean for Graduate Studies and Research, College of Engineering and Science

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Gray, Harry J., Jr., Professor of Electrical Engineering and Science

Hameka, Hendrik F., Professor of Chemistry

Harris, A. Brooks, Professor of Physics

Heeger, Alan J., Professor of Physics and Director of the Laboratory for Research on the Structure of Matter

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Wayland, Bradford B., Associate Professor of Chemistry

Worrell, Wayne L , Professor of Metallurgy and Materials Science

Zemel, Jay N., RCA Professor of Solid State Electronics and Chairman of Electrical Engineering and Science

LRSM AFFILIATED FACULTY

Callen, Herbert B., Professor of Physics

Korostoff, Edward, Associate Professor of Biomaterials in Dental Medicine and Metallurgy and Materials Science

Pollack, Solomon R., Associate Professor of Metallurgy and Materials Science

Thompson, Thomas E., Assistant Professor of Electrical Engineering and Science

White, David, Professor and Chairman of Chemistry

VII. DEGREES GRANTED

Master's Degrees Conferred in the Materials Sciences August 1974 to May 1975

Andrea K. Cianelli (Metallurgy and Materials Science). "Temper Embrittlement of a Nickel-Chromium Steel by Tin and Phosphorus". Thesis Director: Dr. C. J. McMahon, Jr.

Daniel R. DiMicco (Metallurgy and Materials Science). "The Temperature Dependence of the Macroscopic Yield Stress and the Saturation Magnetization in Ir_3Cr". Thesis Director: Dr. D. P. Pope

Howard H. Liebermann (Metallurgy and Materials Science). "Plastic and Magnetoplastic Deformation Modes in Dysprosium Single Crystals". Thesis Director: Dr. C. D. Graham, Jr.

Marilyn L. Sessions (Metallurgy and Materials Science). "The Effect of an Air Environment on the Stress Rupture Behavior of Cast Udimet 700". Thesis Director: Dr. C. J. McMahon, Jr.

Hirowo G. Suzuki (Metallurgy and Materials Science). "Quantification of Auger Electron Spectroscopy". Thesis Director: Dr. C. J. McMahon, Jr.

Doctor of Philosophy Degrees Conferred
in the Materials Sciences
August 1974 to May 1975

James C. Bremer (Physics). "Nuclear Magnetic Resonance Study of Cobalt-59 Impurities in High-Temperature Aluminum-Copper Hosts". Thesis Director: Dr. J. A. Gardner, Jr.

Gerard J. Bunick (Chemistry). "Studies on Yeast Inorganic Pyrophosphatase and the Crystal and Molecular Structure of 9-β-D-Arabinofuranosyladenine". Thesis Director: Dr. D. H. Voet

Raul G. Coltters (Metallurgy and Materials Science). "The Development of a High-Temperature Carbide Electrolyte". Thesis Director: Dr. G. R. Belton

Geoffrey M. T. Foley (Physics). "Magneto-Plasma Studies of the Lattice and Electronic Properties of Lead Telluride". Thesis Director: Dr. D. N. Langenberg

Richard V. Gutowski (Chemistry). "Energy Transfer in the Nitrogen Afterglow". Thesis Director: Dr. W. R. Brennen

Cheng-cher Huang (Physics). "Optical Studies on Phase Transitions". Thesis Director: Dr. J. T. Ho

David Kalkstein (Physics). "A Green's Function Theory of Electronic Properties at Solid Surfaces". Thesis Director: Dr. P. Soven

Satish K. Khanna (Physics). "Microwave Studies of the Metallic State and Metal-Insulator Transition in the One-Dimensional Organic Conductor (TTF)(TCNQ)". Thesis Director: Dr. A. J. Heeger

Martha L. Law (Chemistry). "Comparison of Argon-Argon Interatomic Potentials from Elastic Molecular Beam Scattering Data". Thesis Director: Dr. D. D. Fitts

Ta-Yuen Li (Chemistry). "Triplet Exciton Band Structure Studies of Molecular Crystals". Thesis Director: Dr. R. M. Hochstrasser

Peter J. Meschter (Metallurgy and Materials Science). "An Investigation of High-Temperature Thermodynamic Properties in the Pt-Ti, Pt-Zr, and Pt-Hf Systems". Thesis Director: Dr. W. L. Worrell

Robert A. Mulford (Metallurgy and Materials Science). "The Embrittlement of Ni-Cr Steels by Phosphorus and Antimony". Thesis Director: Dr. D. P. Pope

Zdenka Novosad (Chemistry). "Spectroscopic and Magnetic Resonance Studies of Aromatic Molecules". Thesis Director: Dr. R. M. Hochstrasser

Larry W. Olson (Chemistry). "Small Molecule Complexes of Iron and Manganese Porphyrins". Thesis Director: Dr. B. B. Wayland

Ronald S. Pindak (Physics). "An Experimental Study of Pretransitional Effects near Nematic to Smectic-A Liquid Crystal Phase Transitions". Thesis Director: Dr. J. T. Ho

Syamal K. Poddar (Chemical and Biochemical Engineering). "Chain Dimension and Dilute Solution Behavior of Poly(1, 4-Dichloro-2, 3-Epoxybutane)s". Thesis Director: Dr. W. C. Forsman

Eugene F. Rybaczewski (Physics). "Nuclear Spin-Lattice Relaxation Studies in Highly Conducting Organic Molecular Solids". Thesis Director: Dr. A. J. Heeger

Christopher Scopazzi (Chemistry). "Nuclear Spin-Lattice Relaxation in the Ordered State of Solid Deuterium". Thesis Director: Dr. D. White

John C. Scott (Physics). "The Magnetic Properties of One Dimensional Systems: TTF-TCNQ and Poly(Metal Phosphinates)". Thesis Director: Dr. A. J. Heeger

Elliot B. Slutsky (Electrical Engineering and Science). "Geometric Effects on the Gate Controlled Capacitor". Thesis Director: Dr. J. N. Zemel

William C. Stallings, Jr. (Chemistry). "The Crystal and Molecular Structures of Hexadecamethylbicyclo[3. 3. 1]Nonasilane, D-(+)-Biotin and Tricarbonyl-[1, 2, 2a, 12a-η-5, 10-Dimethyldibenzo[a, c] Cyclobuta[f]Cyclooctene-3, 12-Dione]Iron". Thesis Director: Dr. J. Donohue

Elliott J. Sutow (Metallurgy and Materials Science). "An In Vitro Investigation of the Anodic Dissolution and Capacitance Behavior of 316-L Stainless Steel as Surgical Orthopedic Implant Material". Thesis Director: Dr. E. Korostoff

Shinji Takayama (Metallurgy and Materials Science). "Deformation and Fracture of the Nickel-Palladium-Phosphorus Amorphous Alloys". Thesis Director: Dr. R. Maddin

Destination of Graduates
August 1974 to May 1975

Bremer, James C., Member, Technical Staff, General Research Company

Bunick, Gerard J., Postdoctoral, University of Pennsylvania

Coltters, Raul G., Associate Professor, Venezolano de Investigaciones Cientificas, Caracas

Foley, Geoffrey M. T., Postdoctoral, University of Pennsylvania

Gutowski, Richard V., Research Staff, Pennwalt Corporation

Huang, Cheng-cher, Postdoctoral, University of Illinois

Kalkstein, David, Enrolled in Medical School

Khanna, Satish K., Postdoctoral, University of Pennsylvania

Law, Martha L., Postdoctoral, University of Denver

Li, Ta-Yuen, Postdoctoral, University of Michigan

Meschter, Peter J., Postdoctoral, Max-Planck Institute for Iron and Steel Making

Mulford, Robert A., Assistant Scientist, Argonne National Laboratory

Novosad, Zdenka, Research Associate, Baylor College of Medicine

Olson, Larry W., Postdoctoral, University of Illinois

Pindak, Ronald S., Postdoctoral, Harvard University

Poddar, Syamal K., Postdoctoral, University of Pennsylvania

Rybaczewski, Eugene F., Postdoctoral, Massachusetts Institute of Technology

Scopazzi, Christopher, Research Chemist, DuPont

Scott, John C., Assistant Professor, Cornell University

Slutsky, Elliot B., Research Engineer, Bell Telephone Laboratory

Stallings, William C., Jr., Research Associate, Institute for Cancer Research

Sutow, Elliott J., Lecturer, Dalhousie University

Takayama, Shinji, Research Scientist, Allied Chemical Corporation

VIII. PUBLICATIONS

Agarwal, D. P. and Gaskell, D. R., "The Self Diffusion of Iron in Fe_2SiO_4 and $FeCaSiO_4$ Melts", Met. Trans. (Accepted)

Anderson, R. W., Jr., Hochstrasser, R. M., Lutz, H. and Scott, G. W., "Direct Measurements of Energy Transfer between Triplet States of Molecules in Liquids Using Picosecond Pulses", J. Chem. Phys. 61, 7, 2500 (1974)

Anderson, R. W., Jr., Hochstrasser, R. M., Lutz, H. and Scott, G. W., "Direct Measurements of Internal Conversion between Excited Electronic States of a Molecule in the Condensed Phase", Chem. Phys. Lett. 32, 204 (1975)

Anderson, R. W., Hochstrasser, R. M., Lutz, H. and Scott, G. W., "Measurements of Intersystem Crossing Kinetics Using 3545 Å Picosecond Pulses: Nitronaphthalenes and Benzophenone", Chem. Phys. Lett. 28, 153 (1974)

Aspnes, D. E. and Fischer, J. E., "Modulation Spectroscopy", Academic Press (Accepted)

Aspnes, D. E. and Fischer, J. E., "Modulation Spectroscopy", in Encyclopedia Dictionary of Physics, Ed., J. Thewlis, Pergamon Press (Accepted)

Aymeloglu, S. and Zemel, J. N., "Freeze-Out Effects on N-Channel MOSFET's", Second Annual Conf. of the Physics of Compound Semiconductor Interfaces

Bald, J. F., Jr., Sharp, K. G. and MacDiarmid, A. G., "The Isolation and Characterization of Pentafluorodisilane", J. Fluorine Chem. 3, 433 (1974)

Barmatz, M., Testardi, L. R., Garito, A. F. and Heeger, A. J., "Elastic Properties of One-Dimensional Compounds", Solid State Commun. 15, 1299 (1974)

Belton, G. R., Choudary, U. V. and Gaskell, D. R., "Thermodynamics of Mixing in Molten Sodium-Potassium Silicates", Physical Chemistry of Process Metallurgy, The Richardson Conference, I. M. M. London (1974) p. 247

Boggs, R. and Donohue, J., "Spermine Copper(II) Perchlorate", Acta Cryst. B31, 320 (1975)

Bray, R. G., Hochstrasser, R. M. and Sung, H. N., "Two-Photon Excitation Spectra of Molecular Gases: New Results for Benzene and Nitric Oxide", Chem. Phys. Lett. 33, 1 (1975)

Bray, R. C., Hochstrasser, R. M. and Wessel, J. E., "Continuously Tunable Two-Photon Excitation of Individual Rotational Levels of the $A^2\Sigma^+$ State of Nitric Oxide", Chem. Phys. Lett. 27, 2, 167 (1974)

Brennen, W., Gutowski, R. V. and Shane, E. C., "Vibrational Distributions of $N_2(A^3\Sigma_u^+)$ in the Nitrogen Afterglow", Chem. Phys. Lett. 27, 138 (1974)

Brennen, W. and Shuman, M. E., "A New Example of Formal Non-Steady-State Kinetics. A Model of Heterogeneous Atom Recombination", J. Phys. Chem. 79, 741 (1975)

Bright, A. A., Chaikin, P. M. and McGhie, A. R., "Photoconductivity and Small Polaron Effects in Tetracyanoquinodimethan", Phys. Rev. 10, 3560 (1974)

Bright, A. A., Cohen, M. J., Garito, A. F., Heeger, A. J., Mikulski, C. M. and MacDiarmid, A. G., "Epitaxial Crystalline Films of the Metallic Polymer: $(SN)_x$", Appl. Phys. Lett. 26, 612 (1975)

Bright, A. A., Cohen, M. J., Garito, A. F., Heeger, A. J., Mikulski, C. M., Russo, P. J. and MacDiarmid, A. G., "Optical Reflectance of Polymeric Sulfur Nitride Films from the Ultraviolet to the Infrared", Phys. Rev. Lett. 34, 206 (1975)

Bright, A. A., Garito, A. F. and Heeger, A. J., "Optical Conductivity Studies in a One-Dimensional Organic Metal: Tetrathiofulvalene Tetracyanoquinodimethan (TTF)(TCNQ)", Phys. Rev. B 10, 1328 (1974)

Brooks, M. S. S. and Egami, T., "Magnetic Anisotropy of the Heavy Rare Earths", AIP Conf. Proc. 18, 1258 (1974)

Brooks, M. S. S. and Egami, T., "Renormalization of the Magnon-phonon Interaction in HCP Ferromagnets", J. Phys. C; Solid St. Phys. 7, 3594 (1974)

Brown, N. and Fischer, S., "Nucleation and Growth of Crazes in Amorphous Polychlorotrifluoroethylene in Liquid Nitrogen", J. of Polymer Sci. 13, 1315 (1975)

Brown, N. and Imai, Y., "The Yielding of Polycarbonate in a Nitrogen Environment at Low Pressures and Temperatures", J. Poly. Sci. Lett. (Accepted)

Brown, N. and Parrish, M. F., "Environmental Crazing and Fracture of Polymers in Nitrogen, Argon, and Helium", Recent Advances in Science and Technology of Materials, Ed., A. Bishay, Plenum Press, Vol. 2 (1974) p. 1

Buchner, S. and Burstein, E., "Raman Scattering by Wave-Vector--Dependent LO-Phonon--Plasmon Modes in n-InAs", Phys. Rev. Lett. 33, 908 (1974)

Buckner, S. A. and Langenberg, D. N., "Temperature Dependence of the Riedel Singularity", Low Temperature Physics-LT 13, Vol. III, p. 285, Eds., K. D. Timmerhaus, W. J. O'Sullivan and E. F. Hammel, Plenum Press, New York (1974)

Bunick, G., McKenna, G. P., Colton, R. and Voet, D., "The X-Ray Structure of Yeast Inorganic Pyrophosphatase, Crystal Data", J. Biol. Chem. 249, 4647 (1974)

Bunick, G. and Voet, D., "Crystal and Molecular Structure of 9-β-D-Arabinofuranosyladenine", Acta Cryst. B30, 1651 (1974)

Burstein, E., Chen, W., Chen, Y. J. and Hartstein, A., "Surface Polaritons: Propagating Electromagnetic Modes at Interfaces", J. Vac. Sci. and Tech. 11, 1004 (1974)

Calabrese, C. and Laird, C., "Comments on Cyclic Response of Two Phase Alloys", Mat. Sci. and Eng. 15, 95 (1974)

Calabrese, C. and Laird, C., "High Strain Fatigue Fracture Mechanisms in Two Phase Alloys", Met. Trans. 5, 1785 (1974)

Callen, H., "Thermodynamics as a Science of Symmetry", Foundations of Physics 4, 423 (1974)

Chen, J. T. and Langenberg, D. N., "Fine Structure in the Anomalous DC Current Singularities of a Josephson Tunnel Junction", Low Temperature Physics-LT 13, Vol. III, p. 289, Eds., K. D. Timmerhaus, W. J. O'Sullivan, and E. F. Hammel, Plenum Press, New York (1974)

Chen, Y. J., Burstein, E. and Mills, D. L., "Raman Scattering by Surface Polaritons", Phys. Rev. Lett. 34, 1516 (1975)

Chi, C-K. and Nixon, E. R., "Resonance Raman Studies of RbTCNQ and KTCNQ", Spectrochimica Acta (Accepted)

Cohen, M. J., Coleman, L. B., Garito, A. F. and Heeger, A. J., "Electrical Conductivity of Tetrathiofulvalinium Tetracyanoquinodimethan (TTF)(TCNQ)", Phys. Rev. B 10, 1298 (1974)

Cohen, M., Khanna, S. K., Gunning, W. J., Garito, A. F. and Heeger, A. J. "Theory of Microwave Losses of One-Dimensional Conductors in the Skin Effect Regime: Application to TTF-TCNQ", Solid State Commun. 17, 367 (1975)

Coleman, L. B., Yamagishi, F. G., Garito, A. F., Heeger, A. J., Dahm, D. J., Miles, M. G. and Wilson, J. D., "TTF-TCNQ: Evidence of Alternating Chains in a Derivative Salt", Phys. Lett. 51A, 412 (1975)

Corsaro, F. A., Solenberger, F. R. and Hameka, H. F., "A Variational Perturbation Treatment of the Hydrogen Molecular-Ion Using the Green Function Method on the United Atom", Intl. J. of Quantum Chem. 8, 319 (1974)

Dahm, A. J. and Langenberg, D. N., "Blackbody Radiation from a Single Mode Source: A Demonstration", Am. J. Phys. (Accepted)

Dahm, A. J. and Langenberg, D. N., "Comments on the Josephson Plasma Resonance in $^3He(A)$", Part IV, Proc. Sanibel Symposia (in press)

Dahm, A. J. and Langenberg, D. N., "Nonlinear Effects in the Josephson Plasma Resonance", J. Low Temp. Phys. 19, 145 (1975)

Davenport, J. W., Einstein, T. L., Soven, P. and Schrieffer, J. R., "Theory of Chemisorption in Relation to Heterogeneous Catalysis", Proc. of the Battelle Colloquium on Physical Basis for Heterogeneous Catalysis, Gstaad, Switzerland, Sept. 1974, Plenum Press, N. Y. (in press)

deTitta, G., Edmunds, G., Stallings, W. and Donohue, J., "The Crystal Structure of Biotin (Vitamin H)", J. Am. Chem. Soc. (in press)

Donohue, J., "Incorrect Crystal Structures: Can They Be Avoided?", Critical Evaluation of Chemical and Physical Structural Information, Eds., D. R. Lide, Jr. and M. A. Paul, Nat. Acad. Sci., Wash. (1974) p. 199

Donohue, J., "Structure of Graphite", Nature 255, 172 (1975)

Donohue, J. and Chesick, J., "The Crystal and Molecular Structure of Dicinnamyl Disulfide", Acta Cryst. (Accepted)

Donovan, T. M., Knotek, M. L. and Fischer, J. E., "Absorption and Transport Studies of Amorphous Ge", in Amorphous and Liquid Semiconductors, Eds., Stuke and Trenig, Halstead, N. Y. (1974) p. 549

Duh, K. Y. and Zemel, J. N., "Properties of PbS Epitaxial Films Grown by a Hot Wall Method", Thin Solid Films 26, 165 (1975)

Egami, T. and Brooks, M. S. S., "Theory of Collective Excitation in Strong Crystal Fields", Proc. of the Conf. on Crystalline Electric Field Effect (Montreal, 1974) (Accepted)

Egami, T. and Brooks, M. S. S., "Unitary Transformation Approach to the Singlet Ground State Problem", AIP Conf. Proc. 18, 1300 (1974)

Egami, T., Flanders, P. J. and Graham, C. D., Jr., "Amorphous Alloys as Soft Magnetic Materials", AIP Conf. Proc. 24 (1975)

Egami, T., Flanders, P. J. and Graham, C. D., Jr., "Low-Field Magnetic Properties of Ferromagnetic Amorphous Alloys", Appl. Phys. Lett. 26, 128 (1975)

Einspahr, H. and Donohue, J., "Crystal and Molecular Structure of μ-Carbonyl-bis-μ-[bis(trifluoromethyl) phosphino)sulfur-P, P']-bis (carbonyl-nickel)", Inorg. Chem. 13, 1839 (1974)

Einstein, T. L., "Changes in Density of States Caused by Chemisorption, with Implications for Photoemission", Sur. Sci. 45, 713 (1974)

Einstein, T. L., "Short-Chain Model of Chemisorption: Exact and Approximate Results", Phys. Rev. B 11, 577 (1975)

Finney, J. M. and Laird, C., "Strain Localization in Cyclic Deformation of Copper Single Crystals", Phil. Mag. 31, 339 (1975)

Fischer, J. E. and Aspnes, D. E., "Modulation Spectroscopy III. Band Structure Analysis", Comments on Solid State Physics 6, 39 (1975)

Flanders, P. J., "Experimental Study of the Twist Viscosity in Nematic Liquid Crystals", Mol. Cryst. Liq. Cryst. 29, 19 (1974)

Flanders, P. J., "Magnetostriction in Some Magnetic Oxide Compacted Powders", IEEE Trans. on Magnetics MAG-10, 1050 (1974)

Flanders, P. J., Egami, T., Gyorgy, E. M. and Van Uitert, L. G., "Field Dependent Magnetic Anisotropy of Some Mixed Garnets with Light Rare Earths", AIP Conf. Proc., Magnetism and Magnetic Materials - 1974 Eds., C. D. Graham, Jr., G. H. Lander and J. J. Rhyne, AIP (1975)

Flanders, P. J., Graham, C. D., Jr. and Egami, T., "Magnetic Properties of Amorphous Alloys", IEEE Trans. on Magnetics (1975) (Accepted)

Friedman, J. M. and Hochstrasser, R. M., "Interference Effects in Resonance Raman Spectroscopy", Chem. Phys. Lett. 32, 414 (1975)

Friedman, J. M. and Hochstrasser, R. M., "Moderately High Resolution Fluorescence Spectrum of the $S_1 \rightarrow S_0$ Transition of Azulene", Chem. Phys. 6, 145 (1974)

Friedman, J. M. and Hochstrasser, R. M., "Time Dependence of the Resonant and Near Resonant Photon Molecular Interactions", Chem. Phys. 6, 155 (1974)

Friedman, J. M. and Hochstrasser, R. M., "The Use of Fluorescence Quenchers in Resonance Raman Spectroscopy", Chem. Phys. Lett. 33, 225 (1975)

Garito, A. F. and Heeger, A. J., "The Design and Synthesis of Organic Metals", Accts. Chem. Res. 7, 232 (1974)

Garito, A. F. and Heeger, A. J., "Tetrathiofulvalinium Tetracyanoquinodimethan (TTF)(TCNQ): A One-Dimensional Organic Metal", Nobel Symposium No. 24, Collective Properties of Physical Systems, Ed., S. Lundquist (Nobel Press 1974)

Goldberg, D. and Belton, G. R., "The Diffusion of Carbon in Iron-Carbon Alloys at 1560°C", Met. Trans. 5, 1643 (1974)

Graham, W. R. and Ehrlich, G., "Direct Identification of Atomic Binding Sites on a Crystal Surface", Sur. Sci. 45, 530 (1974)

Graham, W. R. and Ehrlich, G., "Direct Measurement of the Pair Distribution Function for Adatoms on a Surface", Phys. Rev. Lett. 32, 1309 (1974)

Graham, W. R. and Ehrlich, G., "Surface Diffusion of Atom Clusters", Brit. J. Phys. F 4, 212 (1974)

Graham, W. R. and Ehrlich, G., "Surface Self Diffusion of Single Atoms", Thin Solid Films 25, 85 (1975)

Greenwood, N. N., Savory, C. G., Grimes, R. N., Sneddon, L. G., Davison, A., Wreford, S., "Preparation of a Stable Ferraborane, $B_4H_8Fe(CO)_3$", Chem. Comm. 718 (1974)

Gupta, S. K. and Forsman, W. C., "Statistics of Branched, Random-Flight Chains", Macromolecules 7, 853 (1974)

Gupta, S. K., Shah, V. R. and Forsman, W. C., "Molecular Relaxation of Nearly Monodisperse Polystyrene Melts", Macromolecules 7, 948 (1974)

Gustafsson, T., Brodén, G. and Nilsson, P. O., "Photoelectric Properties of Evaporated Be Films", J. Phys. F (Accepted)

Egami, T. and Brooks, M. S. S., "Theory of Collective Excitation in Strong Crystal Fields", Proc. of the Conf. on Crystalline Electric Field Effect (Montreal, 1974) (Accepted)

Egami, T. and Brooks, M. S. S., "Unitary Transformation Approach to the Singlet Ground State Problem", AIP Conf. Proc. 18, 1300 (1974)

Egami, T., Flanders, P. J. and Graham, C. D., Jr., "Amorphous Alloys as Soft Magnetic Materials", AIP Conf. Proc. 24 (1975)

Egami, T., Flanders, P. J. and Graham, C. D., Jr., "Low-Field Magnetic Properties of Ferromagnetic Amorphous Alloys", Appl. Phys. Lett. 26, 128 (1975)

Einspahr, H. and Donohue, J., "Crystal and Molecular Structure of μ-Carbonyl-bis-μ-[bis(trifluoromethyl) phosphino sulfur-P, P'] -bis (carbonyl-nickel)", Inorg. Chem. 13, 1839 (1974)

Einstein, T. L., "Changes in Density of States C- sed by Chemisorption, with Implications for Photoemission", Sur. Sci. 45, 713 (1974)

Einstein, T. L., "Short-Chain Model of Chemisorption: Exact and Approximate Results", Phys. Rev. B 11, 577 (1975)

Finney, J. M. and Laird, C., "Strain Localization in Cyclic Deformation of Copper Single Crystals", Phil. Mag. 31, 339 (1975)

Fischer, J. E. and Aspnes, D. E., "Modulation Spectroscopy III. Band Structure Analysis", Comments on Solid State Physics 6, 39 (1975)

Flanders, P. J., "Experimental Study of the Twist Viscosity in Nematic Liquid Crystals", Mol. Cryst. Liq. Cryst. 29, 19 (1974)

Flanders, P. J., "Magnetostriction in Some Magnetic Oxide Compacted Powders", IEEE Trans. on Magnetics MAG-10, 1050 (1974)

Flanders, P. J., Egami, T., Gyorgy, E. M. and Van Uitert, L. G., "Field Dependent Magnetic Anisotropy of Some Mixed Garnets with Light Rare Earths", AIP Conf. Proc., Magnetism and Magnetic Materials - 1974 Eds., C. D. Graham, Jr., G. H. Lander and J. J. Rhyne, AIP (1975)

Flanders, P. J., Graham, C. D., Jr. and Egami, T., "Magnetic Properties of Amorphous Alloys", IEEE Trans. on Magnetics (1975) (Accepted)

Friedman, J. M. and Hochstrasser, R. M., "Interference Effects in Resonance Raman Spectroscopy", Chem. Phys. Lett. 32, 414 (1975)

Friedman, J. M. and Hochstrasser, R. M., "Moderately High Resolution Fluorescence Spectrum of the $S_1 \rightarrow S_0$ Transition of Azulene", Chem. Phys. 6, 145 (1974)

Friedman, J. M. and Hochstrasser, R. M., "Time Dependence of the Resonant and Near Resonant Photon Molecular Interactions", Chem. Phys. 6, 155 (1974)

Friedman, J. M. and Hochstrasser, R. M., "The Use of Fluorescence Quenchers in Resonance Raman Spectroscopy", Chem. Phys. Lett. 33, 225 (1975)

Garito, A. F. and Heeger, A. J., "The Design and Synthesis of Organic Metals", Accts. Chem. Res. 7, 232 (1974)

Garito, A. F. and Heeger, A. J., "Tetrathiofulvalinium Tetracyanoquinodimethan (TTF)(TCNQ): A One-Dimensional Organic Metal", Nobel Symposium No. 24, Collective Properties of Physical Systems, Ed., S. Lundquist (Nobel Press 1974)

Goldberg, D. and Belton, G. R., "The Diffusion of Carbon in Iron-Carbon Alloys at 1560°C", Met. Trans. 5, 1643 (1974)

Graham, W. R. and Ehrlich, G., "Direct Identification of Atomic Binding Sites on a Crystal Surface", Sur. Sci. 45, 530 (1974)

Graham, W. R. and Ehrlich, G., "Direct Measurement of the Pair Distribution Function for Adatoms on a Surface", Phys. Rev. Lett. 32, 1309 (1974)

Graham, W. R. and Ehrlich, G., "Surface Diffusion of Atom Clusters", Brit. J. Phys. F 4, 212 (1974)

Graham, W. R. and Ehrlich, G., "Surface Self Diffusion of Single Atoms", Thin Solid Films 25, 85 (1975)

Greenwood, N. N., Savory, C. G., Grimes, R. N., Sneddon, L. G., Davison, A., Wreford, S., "Preparation of a Stable Ferraborane, $B_4H_8Fe(CO)_3$", Chem. Comm. 718 (1974)

Gupta, S. K. and Forsman, W. C., "Statistics of Branched, Random-Flight Chains", Macromolecules 7, 853 (1974)

Gupta, S. K., Shah, V. R. and Forsman, W. C., "Molecular Relaxation of Nearly Monodisperse Polystyrene Melts", Macromolecules 7, 948 (1974)

Gustafsson, T., Brodén, G. and Nilsson, P. O., "Photoelectric Properties of Evaporated Be Films", J. Phys. F (Accepted)

Gustafsson, T., Plummer, E. W., Eastman, D. and Freeouf, J., "Interpretation of the Photoelectron Spectra of Molecularly Adsorbed CO", Solid State Comm. 17, 391 (1975)

Hall, W. R. and Hameka, H. F., Erratum: "Second-Order Effect of Spin-Orbit Coupling on the Angular Dependence of the Zero-Field Splitting in CH_2" [J. Chem. Phys. 58, 226 (1973)] J. Chem. Phys. 60, 4104 (1974)

Halperin, B. I. and Lubensky, T. C., "On the Analogy between Smectic A Liquid Crystals and Superconductors", Solid State Commun. 14, 997 (1974)

Hameka, H. F., Quantum Theory of the Chemical Bond, Hafner Press, N. Y. (1975)

Harris, A. B., "Nature of the 'Griffiths' Singularity in Dilute Magnets", Phys. Rev. (Accepted)

Harris, A. B., "Upper Bounds for the Transition Temperatures of Generalized Ising Models", J. Phys. C 1, 3082 (1974)

Harris, A. B. and Lubensky, T. C., "Renormalization-Group Approach to the Critical Behavior of Random-Spin Models", Phys. Rev. Lett. 33, 1540 (1974)

Hartstein, A. and Burstein, E., "Observation of Magneto-Plasmon-Type Surface Polaritons on n-InSb", Solid State Commun. 14, 223 (1974)

Hartstein, A., Burstein, E., Palik, E. D., Kaplan, R., Gammon, R. W. and Henvis, B. W., "Optic Phonon-Magnetoplasmon Type Surface Polaritons on n-InSb", Int. Conf. Phys. Semicond; Stuttgart 1974 (Teubner, Stuttgart, 1974) p. 541

Heeger, A. J. and Garito, A. F., "The Electronic Properties of TTF-TCNQ", Low-Dimensional Cooperative Phenomena, Ed., H. J. Keller, Plenum Publishing Corporation 1975, p. 89

Hochstrasser, R. M., "Some Aspects of Energy Transfer in the Organic Solid State", in Energy Transfer, Eds., Levine and Jortner, Academic Press (1975) (Accepted)

Hochstrasser, R. M., "Triplet Excitons", MTP Int. Rev. Sci., Eds., Ramsay and Buckingham, Butterworth (1975) (Accepted)

Hochstrasser, R. M. and King, D. S., "Absorption, Fluorescence and Phosphorescence Spectra of the Singlet and Triplet States of s-Tetrazine in the Crystal and in Mixed Crystals at Low Temperatures", Chem. Phys. 5, 439 (1974)

Hochstrasser, R. M., Li, T-Y., Sung, H-N., Wessel, J. and Zewail, A. H., "Experimental Studies of Triplet Exciton Bands of Molecular Crystals", Pure Appl. Chem. 37, 85 (1974)

Hochstrasser, R. M. and Wessel, J. E., "Time Resolved Fluorescence of Anthracene in Mixed Crystals at 2 K", Chem. Phys. Lett. 6, 19 (1974)

Hochstrasser, R. M. and Zewail, A. H., "Optical and Magnetic Resonance Spectra of Linear Chain Excitons", Chem. Phys. 4, 142 (1974)

Holcomb, W. and Harris, A. B., "Spin Waves in Dilute Antiferromagnets", A. I. P. Conf. Proc. (Magnetism Conference, 1974) (Accepted)

Huang, C. C., Pindak, R. S., Flanders, P. J. and Ho, J. T., "Dynamics of Freedericksz Deformation near a Nematic-Smectic-A Transition", Phys. Rev. Lett. 33, 400 (1974)

Huang, C. C., Pindak, R. S. and Ho, J. T., "Birefringence and Order Parameter in Nematic N-p-Cyanobenzylidene-p-Octyloxyaniline", J. Phys. (Paris) 35, L-185 (1974)

Jacobsen, C. S., Tanner, D. B., Garito, A. F. and Heeger, A. J., "Single-Crystal Reflectance Studies of Tetrathiafulvalene Tetracyanoquinodimethane", Phys. Rev. Lett. 33, 1559 (1974)

Kang, S. K. and Laird, C., "Precipitation in Thin Foils of Al-4w/o Cu Alloy, I: Morphology, Crystallography and Interfacial Structure of θ Precipitates", Acta Met. 22, 1481 (1974)

Kang, S. K. and Laird, C., "Precipitation in Thin Foils of Al-4w/o Cu Alloy, II: Growth Kinetics of θ Precipitates", Acta Met. 23, 35 (1975)

Kar, N. and Soven, P., "Band Structure of Thin Films", Phys. Rev. B 11, 3761 (1975)

Khanna, S. K., Bright, A. A., Garito, A. F. and Heeger, A. J., "Evidence of Strong Coulomb Interactions in Alkali-TCNQ Salts", Phys. Rev. B 10, 2139 (1974)

Khanna, S. K., Ehrenfreund, E., Garito, A. F. and Heeger, A. J., "Microwave Properties of High Purity Tetrathiofulvalene-Tetracyanoquinodimethan (TTF-TCNQ)", Phys. Rev. B 10, 2205 (1974)

Khanna, S. K., Garito, A. F., Heeger, A. J. and Jaklevic, R. C., "Anisotropic Dielectric Constant of TTF-TCNQ Observed by Dielectric Resonance", Solid State Commun. 16, 667 (1975)

Kim, H-W. and Hameka, H. F., "Calculation of the Rotational Magnetic Moment of the Hydrogen Molecule", Chem. Phys. Lett. (Accepted)

Kim, Y-W. and Belton, G. R., "The Thermodynamics of Volatilization of Chromic Oxide: Part I. The Species CrO_3 and CrO_2OH", Met. Trans. 5, 1811 (1974)

Kirkpatrick, S. and Harris, A. B., "Static Properties of Dilute Ferri- and Antiferromagnets", A.I.P. Conf. Proc. (Magnetism Conference, 1974) (Accepted)

Kiselev, V. D. and Miller, J. G., "Experimental Proof that the Diels-Alder Reaction of Tetracyanoethylene with 9,10-Dimethylanthracene Passes through Formation of a Complex between the Reactants", J. Am. Chem. Soc. 97, 4036 (1975)

Krumhansl, J. A. and Schrieffer, J. R., "Dynamics and Statistical Mechanics of a One-Dimensional Model Hamiltonian for Structural Phase Transitions", Phys. Rev. B 11, 3535 (1975)

Kwak, J. F., Chaikin, P. M., Russel, A. A., Garito, A. F. and Heeger, A. J., "Anisotropic Thermopower of TTF-TCNQ", Solid State Commun. (Accepted)

Laird, C., "Alloy Design for Fatigue Resistance", ASM Materials Science Symposium, Oct. 1974, Eds., G. S. Ansell and J. K. Tien, ASM (Accepted)

Laird, C., Chapter on "Electron Microscopy" in Characterisation of Solid Surfaces, Eds., P. F. Kane and G. B. Larrabee, Texas Inst. Co., Inc. (1974)

Laird, C., "Cyclic Deformation of Metals and Alloys", in Plastic Deformation of Materials, Ed., R. J. Arsenault, Academic Press (Accepted)

Laird, C., Finney, J. M., Schwartzman, A. and de la Veaux, R., "History Dependence in the Cyclic Stress-Strain Response of Wavy Slip Materials", J. Testing and Evaluation (Accepted)

Lakshmikantham, M. V., Cava, M. P. and Garito, A. F., "Organic Metals: Synthesis of sym-Diselenadithiofulvalene", Chem. Commun. (1975) (in press)

Langenberg, D. N., "Characteristic Times in Superconductors", in Festkörperprobleme-Advances in Solid State Physics, Vol. XIV, p. 67, Ed., H. J. Queisser, F. Vieweg & Sohn, Braunschweig (1974)

Law, M. L. and Fitts, D. D., "Comparison of Argon-Argon Interatomic Potentials from Elastic Molecular-Beam Scattering Data", Mol. Phys. 29, 1933 (1975)

Leibson, A. and Plummer, E. W., "Theory of Angular Dependence of Photoemission UHE Shapes from Adsorbates", J. Chem. Soc. Faraday II (1975) (Accepted)

Liebsch, A., "Theory of Angular Resolved Photoemission from Adsorbates", Phys. Rev. Lett. 32, 1203 (1974)

Liebsch, A. and Plummer, E. W., "Theory of the Angular Dependence of the Photoemission Line Shape from an Adsorbate, Faraday Disc. Chem. Soc. No. 58 (1975)

Lopez, A., Duh, D. and Zemel, J. N., "Deep Impurity Levels in Epitaxial PbS Films", Mater. Sci. and Eng. 17, 63 (1975)

Loughin, S., Yang, C. Y., and Fischer, J. E., "On-Line Data Reduction with a Prism Spectrometer, Appl. Optics 14, 1373 (1975)

Lubensky, T. C., "Critical Properties of Random-Spin Models from the ϵ-*Expansion*", *Phys.* Rev. B 11, 3573 (1975)

Lubensky, T. C., "Latent Heat of the Cholesteric to Smectic A Transition", J. Physique (Paris) (Accepted)

Lubensky, T. C. and Harris, A. B., "Critical Properties of Random Spin Systems Using the Renormalization Group", A. I. P. Conf. Proc. (1974 Magnetism Conference) (Accepted)

Lubensky, T. C. and Harris, A. B., "Effect of Randomness on Critical Behavior of Spin Models", Proc. of the 1974 MMM Conf. (Accepted)

Lubensky, T. C. and Rubin, M. H., "Critical Phenomena in Semi-Infinite Systems I: ϵ-Expansion for Positive Extrapolation Length", Phys. Rev. B 11, 4533 (1975)

Lubensky, T. C. and Rubin, M. H., "Critical Phenomena in Semi-Infinite Systems II: Mean Field Theory", Phys. Rev. (Accepted)

MacDiarmid, A. G., Mikulski, C. M., Saran, M. S., Russo, P. J., Cohen, M. J., Bright, A. A., Garito, A. F. and Heeger, A. J., "Synthesis and Selected Properties of Polymeric Sulfur Nitride, $(SN)_x$", Proc. of Symposium on Inorganic Solids with Unusual Electronic Properties (Accepted)

Madden, W. G. and Fitts, D. D., "Integral-Equation Perturbation Theory for the Radial Distribution Function of Simple Fluids", Mol. Phys. (Accepted)

Madden, W. G. and Fitts, D. D., "A New Perturbation Technique for the Radial Distribution Function of Simple Fluids", Mol. Phys. 28, 1095 (1974)

Madden, W. G. and Fitts, D. D., "On the Calculation of a Corrected Radial Distribution Function", J. Chem. Phys. 61, 4935 (1974)

Madden, W. G. and Fitts, D. D., "Perturbation Theory for the Radial Distribution Function for Simple Polar Fluids", Chem. Phys. Lett. 28, 427 (1974)

Madden, W. G. and Fitts, D. D., "A Re-examination of the HNC Theory for the Radial Distribution Function", J. Chem. Phys. 61, 5475 (1974)

Maddin, R., "Early Iron Metallurgy in the Near East", Trans. Iron and Steel Institute of Japan 15, 2, 59 (1975)

Magee, C. P., Sneddon, L. G., Beer, D. C. and Grimes, R. N., "Bridge Insertion Reactions of the 2,3-$C_2B_4H_5$-Ion with Aluminum Gallium and Transition Metal Reagents", J. of Orgmet. Chem. 86, 159 (1975)

Masumoto, T. and Maddin, R., "Structural Stability and Mechanical Properties of Amorphous Alloys", Mat. Sci. and Eng. 19, 1 (1975)

McGhie, A. R., "An All Glass Apparatus for 'Continuous' Chromatography and Its Application to Chrysene", Mol. Cryst. Liq. Cryst. 27, 431 (1974)

McGhie, A. R., Garito, A. F. and Heeger, A. J., "A Gradient Sublimer for Purification and Crystal Growth of Thermally Unstable Organic Compounds", J. Cryst. Growth 22, 295 (1974)

McMahon, C. J., Jr., "Embrittlement of Alloy Steels by Impurities", Conf. on the Mechanics and Physics of Fracture, Churchill College, Cambridge, Jan. 1974

McMahon, C. J., Jr., "The Strength of Grain Boundaries in Metals and Alloys", Conf. on Grain Boundaries in Engineering Materials, Bolton Landing, N. Y., June 1974

Mehne, L. F. and Wayland, B. B., "Properties of Ni(diphenylglyoximota)$_2$X (X = Br, I) in the Presence of Donor Molecules and in the Solid", Inorg. Chem. (Accepted)

Meschter, P. J. and Worrell, W. L., "Evaluation of an NbO, $Nb_2O_{4.8}$ Reference Electrode for Emf Measurements at Low Oxygen Activities", Met. Trans. 6, 345 (1975)

Mikulski, C. M., Russo, P. J., Saran, M. S., Garito, A. F., Heeger, A. J. and MacDiarmid, A. G., "Synthesis and Structure of the Polymeric Metal, $(SN)_x$, and Its Precursor, S_2N_2", Chem. Commun. 476 (1975)

Mikulski, C. M., Saran, M. S., Russo, P. J., Cohen, M. J., Bright, A. A., Garito, A. F. and Heeger, A. J., "Synthesis and Selected Properties of Polymeric Sulfur Nitride, $(SN)_x$" in Advances in Chemistry, Ed., R. B. King, Am. Chem. Soc. (Accepted)

Mills, D. L. and Burstein, E., "Polaritons: The Electromagnetic Modes of Media", Reports on Progress in Physics 37, 817 (1974)

Mindel, M. J. and Brown, N., "Creep, Recovery and Fatigue in Polycarbonate", J. of Mat. Sci. 9, 1661 (1974)

Murgich, J., "Nuclear Quadrupole Resonance of ^{14}N in Cubic Tetracyanoethylene", Chem. Phys. Lett. 18, 420 (1974)

Murgich, J. and Pissanetzky, S., "Temperature Dependence of the ^{14}N Nuclear Quadrupole Resonance and the Observation of the Phase Transition in Cubic Tetracyanoethylene", J. Chem. Phys. 62, 92 (1975)

Myers, A. L., Bonacci, J. C. and Eagleton, L. C., "The Evaporation and Condensation Coefficient of Water, Ice and Carbon Tetrachloride", Chem. Eng. Sci. (Accepted)

Myers, A. L. and Glandt, E., "Thermochemical Production of Hydrogen by Decomposition of Water", Ind. Eng. Chem., Process R & D (Accepted)

Myers, A. L. and Seider, W. D., Introduction to Chemical Engineering and Computer Calculations, Prentice-Hall (1975) (Accepted)

Nilsson, P. O., Arbman, G. and Gustafsson, T., "The Energy Band Structure and Spectroscopic Properties of Beryllium", J. Phys. F 4, 1937 (1974)

Ohtani, H. and McMahon, C. J., Jr., "Modes of Fracture in Temper Embrittled Steels", Acta Met. (Accepted)

Ozawa, K., Flanders, P. J. and Graham, C. D., Jr., "Characterization of Magnetic Recording Tape with the Rotating-Sample Magnetometer", IEEE Trans. Magnetics, MAG-10, 663 (1974)

Paulson, R. H and Schrieffer, J. R., "Induced Covalent Bond Theory of Chemisorption", Sur. Sci. 48, 329 (1975)

Pedersen, N. F., Finnegan, T. F. and Langenberg, D. N., "Evidence for the Existence of the Josephson Quasiparticle-Pair Interference Current", Low Temperature Physics-LT 13, Vol. III, p. 268, Eds., K. D. Timmerhaus, W. J. O'Sullivan and E. F. Hammel, Plenum Press, New York (1974)

Perov, P. I. and Fischer, J. E., "Thermoreflectance of TTF:TCNQ", Phys. Rev. Lett. 33, 521 (1974)

Physics of IV-VI Compounds and Alloys, Ed., S. Rabii, Gordon and Breach, 1975

Pinczuk, A. and Burstein, E., "Fundamentals of Inelastic Light Scattering in Solids", Ed., M. Cordona, Springer Verlag (Accepted)

Plummer, E. W., "The Applicability of Electron Emission Spectroscopies to Elucidate Chemisorption", Physical Basis for Heterogeneous Catalysis, Gstaad Swi'., Sept. 1974, Published in Battelle Colloquium

Plummer, E. W., "Experimental Observations of Electronic Energy Levels at a Solid-Vacuum Interface", J. Electrochem. Soc. 121, 1186 (1974)

Plummer, E. W., "Field Emission Work Function", Sur. Sci. 48, 417 (1975)

Plummer, E. W., "Photoemission and Field Emission Electron Spectroscopies", Topics in Applied Physics, Ed., R. Comer, Springer-Verlag (1975)

Plummer, E. W., Gadzuk, J. W. and Penn, D. R., "Vacuum-Tunneling Spectroscopy", Phys. Today 28, 63 (1975)

Plummer, E. W., Waclawski, B. J. and Vorburger, T., "Photoelectron Spectra of the Decomposition of Ethylene on (110)W", Chem. Phys. Lett. 28, 510 (1974)

Rabii, S., "Effect of Strain on the Secondary Band Extrema of PbS, PbSe, PbTe, and SnTe", Phys. Rev. B7, 3830 (1973)

Rabii, S. and Lasseter, R. H, "Band Structure of PbPo and Trends in the Pb Chalcogenides", Phys. Rev. Lett. 33, 703 (1974)

Rellick, J. R. and McMahon, C. J., Jr., "Intergranular Embrittlement of Iron-Carbon Alloys by Impurities", Met. Trans. 5, 2439 (1974)

Robbins, A., Jeffrey, G. A., Chesick, J. P., Donohue, J., Cotton, F. A., Frenz, B. A. and Murillo, C. A., "A Refinement of the Crystal Structure of Tetraphenyl Methane: Three Independent X-ray Measurements", Acta Cryst. (in press)

Rothwarf, A., Sai-Halasz, G. A. and Langenberg, D. N., "Quasiparticle Lifetimes and Microwave Response in Nonequilibrium Superconductors", Phys. Rev. 33, 212 (1974)

Rybaczewski, E. F., Garito, A. F., Heeger, A. J. and Ehrenfreund, E., "Nuclear Spin-Lattice Relaxation and Local Susceptibilities in Tetrathiafulvalene Tetracyanoquinodimethane", Phys. Rev. Lett. 34, 524 (1975)

Sai-Halasz, G. A., Chi, C. C., Denenstein, A. and Langenberg, D. N., "Effects of Dynamic External Pair Breaking in Superconducting Films", Phys. Rev. 33, 215 (1974)

Sandman, D. J. and Garito, A. F., "An Improved Synthetic Route to 11, 11, 12, 12-Tetracyanonaphtho-2, 6-quinodimethan (TNAP)", J. Org. Chem. 39, 1165 (1974)

Sankaran, R. and Laird, C., "Antiphase Domain Boundaries within θ' and η Precipitates", Mat. Sci. and Eng. 15, 159 (1974)

Sankaran, R. and Laird, C., "Effect of Trace Additions of Cd, In and Sn on the Interfacial Structure and Growth Kinetics of θ' Plates in Al-Cu Alloy", Mat. Sci. and Eng. 14, 271 (1974)

Sankaran, R. and Laird, C., "Interfacial Structure of Platelike Precipitates", Phil. Mag. 29, 179 (1974)

Sankaran, R. and Laird, C., "Kinetics of Growth of Platelike Precipitates", Acta Met. 22, 957 (1974)

Sankaran, R. and Laird, C., "The Role of Intruder Dislocations in Modifying the Misfit Dislocation Structures and Growth Kinetics of Precipitate Plates", Met. Trans. 5, 1795 (1974)

Sano, N. and Belton, G. R., "The Thermodynamics of Volatilization of Chromic Oxide: Part II. The Species CrO_2Cl_2", Met. Trans. 5, 2151 (1974)

Schrieffer, J. R., "A New Schema for Entropy", Proc. of the Amer. Philosophical Soc. 118, 538 (1975)

Schrieffer, J. R. and Soven, P., "Electronic Structure of Surfaces", Physics Today (Accepted)

Schrieffer, J. R. and Soven, P., "Surface Physics; Theory of the Electronic Structure", Phys. Today 28, 24 (1975)

Scott, J. C., Garito, A. F. and Heeger, A. J., "Magnetic Susceptibility Studies of Tetrathiofulvalene-Tetracyanoquinodimethan (TTF)(TCNQ) and Related Organic Metals", Phys. Rev. B 10, 3131 (1974)

Scott, J. C., Garito, A. F., Heeger, A. J., Nannelli, P. and Gillman, H. D., "The Magnetic Properties of Poly(Metal Phosphinates): The Effects of Structural Disorder on One-Dimensional Antiferromagnetic Chains", Phys. Rev. B 12, 356 (1975)

Sessions, M. L. and McMahon, C. J., Jr., "The Influence of Stress Components on Intergranular Oxidation and Cracking in a Nickel-Base Superalloy", Conf. on Grain Boundaries in Engineering Materials, Bolton Landing, N. Y., June 1974

Shand, M. L., Ching, L. Y. and Burstein, E., "Raman Scattering by Optical Phonons and Polaritons in CuCl", Solid State Commun. 15, 1209 (1974)

Shieh, H.-S. and Voet, D., "The X-Ray Structure of the Molecular Complex 9-Ethyladenine · Parabanic Acid · Oxaluric Acid Monohydrate", Acta Cryst. (Accepted)

Skelskey, D. A. and Van den Sype, J., "A Relaxation Phenomenon Observed in Fine Gold Wire", Solid State Commun. 15, 1257 (1974)

Smith, A. B., III, "A Vinylogous Wolff Rearrangement; Copper Sulphate-catalysed Decomposition of Unsaturated Diazomethyl Ketones", Chem. Commun. 695 (1974)

Smith, A. B., III and Agosta, W. C., "Photochemical Reactions of 3-Substituted Cyclopentenyl Ketones", J. Am. Chem. Soc. 96, 3289 (1974)

Sneddon, L. G. and Lagow, R. J., "The Reaction of Lithium Vapor with Partially Halogenated Hydrocarbons", Chem. Commun. (Accepted)

Sood, A. K., Yang, C. Y. and Fischer, J. E., "Effect of Cl_2 Exposure on Thermoreflectance of Pb Chalcogenides", Thin Solid Films 16, 1 (1974)

Sood, A. K., Yang, C. Y. and Fischer, J. E., "Effect of Chlorine Exposure on the Thermoreflectance Spectra of Lead Chalcogenide Films", Thin Solid Films 23, 337 (1974)

Stallings, W. and Donohue, J., "The Molecular and Crystal Structure of Permethylbicyclo(3. 3. 1) Nonasilane", Inorg. Chem. (in press)

Suito, H. and Gaskell, D. R., "The Reaction of Water Vapor with Melts in the System VO_2-V_2O_5", Proc. of an International Symposium on Metal-Slag-Gas Reactions and Processes, The Electrochemical Society 1975 (Accepted)

Svendsen, E. N. and Hameka, H. F., "Calculation of the Magneto-Optical Activity of the Hydrogen Molecule", Intl. J. of Quantum Chem. 8, 789 (1974)

Svendsen, E. N. and Hameka, H. F., "Calculation of Molecular Electric Polarizabilities and Dipole Moments. I. General Theory and Application to the Hydrogen Molecule", J. Chem. Phys. 62, 2760 (1975)

Svendsen, E. N. and Hameka, H. F., "Effect of the Rotational Motion of Molecules on Their Optical and Their Magneto-Optical Activity", Intl. J. of Quantum Chem. (Accepted)

Svendsen, E. N. and Hameka, H. F., "On the Perturbation of Molecular Eigenfunctions by a Magnetic Field", Physica 74, 625 (1974)

Takayama, S., "Amorphous Structures: Their Formation and Stability", J. Mat. Sci. (Accepted)

Takayama, S. and Maddin, R., "Fracture of Amorphous Ni-Pd-P Alloys", Phil. Mag. (in press)

Takayama, S. and Maddin, R., "Resistivity Changes by Deformation of Ni-Pd-P Amorphous Alloys", Scripta Met. 9, 343 (1975)

Takayama, S. and Maddin, R., "Rolling and Bending Deformation of Ni-Pd-P Metal Glasses", Acta Met. (Accepted)

Talaat, H. and Burstein, E., "Phase-Matched Electromagnetic Generation and Detection of Surface Elastic Waves on Nonconducting Solids", J. Appl. Phys. 45, 4360 (1974)

Tanner, D. B., Jacobsen, C. S., Garito, A. F. and Heeger, A. J., "Infrared Conductivity of (TTF)(TCNQ) Films", Phys. Rev. Lett. 32, 1301 (1974)

Teichman, R. A. and Nixon, E. R., "The A → X Emission Spectra of PbS and PbSe in Neon Matrices: Enhanced Emission from Isotopes and Matrix Sites", J. Mol. Spectry. 57, 14 (1975)

Teichman, R. A. and Nixon, E. R., "Biphotonic Stimulation of Emission and Matrix Effects in Lead Sulfide in Solid Argon", J. Mol. Spectry. 55, 192 (1975)

Teichman, R. A. and Nixon, E. R., "Vibronic Spectra of Matrix-Isolated Lead Sulfide", J. Mol. Spectry. 54, 78 (1975)

Topp, M. R., "Activation-Controlled Hydrogen Abstraction by Benzophenone Triplet", Chem. Phys. Lett. 32, 144 (1975)

Topp, M. R., "Oscilloscope Display of Picosecond Fluctuations in Light Intensity", Opt. Comm. (Accepted)

Topp, M. R. and Orner, G. C., "Group Dispersion Effects in Picosecond Spectroscopy", Opt. Comm. 13, 276 (1975)

Topp, M. R. and Orner, G. C., "Group Dispersion Effects in Picosecond Spectroscopy: Frequency Dispersion", Chem. Phys. Lett. (Accepted)

Treharne, R. W. and Brown, N., "Factors Influencing the Creep Behavior of Poly(methyl Methacrylate) Cements", J. Biomedical Materials Res. Symp. No. 6, 81 (1975)

Tyler, I. L., Denenstein, A. and Langenberg, D. N., "Infinite-Hold-Time Electronic Ramp Generator", Rev. Sci. Instr. 45, 1007 (1974)

Voet, D., "Intermolecular Interactions in Adenine · Barbiturate Complexes", in Molecular and Quantum Pharmacology, Eds., E. Bergman and B. Pullman, R. Reidel, Dordrecht-Holland, 1975, p. 429

Vogel, F. L., "Electrical Resistivity of Nitrate-Intercalated Graphite Fibers", Proc. 4th London Int'l. Conf. Carbon and Graphite (Accepted)

Vogel, F. L., "Implantation of Carbon in Thin Iron Films", Proc. 4th London Int'l. Conf. Carbon and Graphite (Accepted)

Wayland, B. B. and Abd-Elmageed, M. E., "Phosphorus-31 Hyperfine Coupling in Tetraphenylporphyrin Cobalt(II) Complexes of Trivalent Phosphorus Ligands and Dioxygen Complexes: Substituent Effects on the Phosphorus σ Donor Orbital", J.C.S. Chem. Comm. 61 (1974)

Wayland, B. B. and Abd-Elmageed, M. E., "Tetraphenylporphincobalt(II) Complexes as a Probe for the Nature of Phosphine σ Donor Orbitals: Epr Studies of Phosphine and Dioxygen Complexes", J. Amer. Chem. Soc. 4809 (1974)

Wayland, B. B. and Kapur, V. K., "Epr and Electronic Spectral Evidence for Isomers Resulting from Basal and Axial Ligation of Bis(hexafluoroacetylacetonate)copper(II) by Triphenylphosphine", Inorg. Chem. 13, 2517 (1974)

Wayland, B. B. and Mehne, L. F., "A Comparison of AgMnO with Permanganate and Manganate Salts", Inorg. Nucl. Chem. (1974) (Accepted)

Wayland, B. B., Minkiewicz, J. V. and Abd-Elmageed, M. E., "Spectroscopic Studies for Tetraphenylporphyrin Cobalt(II) Complexes of CO, NO, O_2, RNC and $(RO)_3P$, and a Bonding Model for Complexes of CO, NO, and O_2 with Cobalt(II) and Iron(II) Porphyrins", J. Amer. Chem. Soc. 2795 (1974)

Wayland, B. B. and Olson, L. W., "Low Spin Nitric Oxide Complexes of Manganese Tetraphenylporphyrin", Inorg. Chemica Acta (Accepted)

Wayland, B. B. and Olson, L. W., "Spectroscopic Studies and Bonding Model for Nitric Oxide Complexes of Iron Porphyrins", J. Amer. Chem. Soc. 6037 (1974)

Wolff, S., Smith, A. B., III and Agosta, W. P., "Preparation of Some Bicyclic Ethers", J. Org. Chem. 39, 1607 (1974)

Worrell, W. L., "Developing New Electrochemical Sensors", Proc. of the Int. Symposium on Metal-Slag-Gas Reactions and Processes, Electrochemical Society Meeting, Toronto, Canada; May 11-16, 1975 (Accepted)

Worrell, W. L. and Ramanarayanan, T. A., "Limitations in the Use of Solid-State Electrochemical Cells for High-Temperature Equilibrium Measurements", Cand. Met. Quarterly 13, 325 (1974)

Worrell, W. L. and Ramanarayanan, T. A., "Overvoltage Phenomena in Oxygen-Saturated Copper Electrodes", Met. Trans. 5, 1773 (1974)

Worrell, W. L. and Ramanarayanan, T. A., "A Thermodynamic Investigation of Cubic Sodium Tungsten Bronze, Na_xWO_3", J. Electrochem. Soc. 121, 1530 (1974)

Yeh, J. T. C., "Technique for Fabrication of Superconducting Microbridges and Small Josephson Tunnel Junctions", J. Appl. Phys. 45, 4617 (1974)

Yeh, J. T. C. and Langenberg, D. N., "Observations on Small Tunnel Junctions: Anomalous Critical-Current Temperature Dependence, Periodic Structure, and Microwave Detection", Proc. 1974 Applied Superconductivity Conference, IEEE Trans. Mag., MAG-11, 683 (1975)

Young, J. J. and Zemel, J. N., "Kinetics of the Hydrogen Effect on PbSe Epitaxial Films", Thin Solid Films (Accepted)

Zemel, J. N., "Gas Effects on IV-VI Semiconductor Films", Surface Physics of Phosphors and Semiconductors, Academic Press, London (Accepted)

Zemel, J. N., "Ion-Sensitive Field Effect Transistors and Related Devices", Anal. Chem. 47, 255A (1975)

Zemel, J. N., Rahnamai, H. and Young, J. J., "Gas Effects on Lead Chalcogenides", CRC Reviews (Accepted)

IX. LRSM SEMINAR PROGRAM

Dr. J. Ahearn, Department of Metallurgy and Materials Science, University of Pennsylvania
"Dislocation Structures in III-V Epitaxial Semiconductor Films"

Dr. R. R. Alfano, City University of New York
"The Study of Nonlinear Optical Effects and Transient Phenomena with High Power Picosecond Laser Pulses"

Dr. P. W. Anderson, Bell Telephone Laboratories
"Anisotropic Superfluidity in He^3"

Dr. R. J. Birgeneau, Bell Telephone Laboratories
"Spin Fluctuations in a Two Dimensional Random Antiferromagnet"

Prof. D. C. Bradley, Queen Mary College, London, England
"Low Coordination of Metal Complexes"

Dr. C. Briant, Department of Metallurgy and Materials Science, University of Pennsylvania
"Microclusters: Their Structure, Thermodynamics, and Applications"

Prof. J. K. Brimacombe, University of British Columbia
"Analysis of Metallurgical Processes"

Dr. G. J. Bunick, Chemistry Department, University of Pennsylvania
"X-ray Diffraction Studies of Inorganic Pyrophosphatase"

Dr. L. H. Burck, Northwestern University
"Fatigue Crack Propagation in Fe-Ni and Fe-Mo Single Phase Alloys from 77 to 296 K"

Prof. G. S. Cargill, Yale University
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KEY TO ABBREVIATIONS

ACC	Allied Chemical Company
AFOSR	Air Force Office of Scientific Research
AISI	American Iron and Steel Institute
ARO	Army Research Office
AROD	Army Research Office-Durham
ARPA	Advanced Research Projects Agency
BTL	Bell Telephone Laboratories
GE	General Electric Foundation
IBM	International Business Machines Corporation
KCC	Kennecott Copper Corporation
LRSM	Laboratory for Research on the Structure of Matter
MOC	Mobil Oil Corporation
MOS	MOS Technology
MPC	Metal Properties Council
NASC	Naval Air Systems Command
NATO	North Atlantic Treaty Organization
NBS	National Bureau of Standards
NIGMS	National Institute of General Medical Sciences
NIH	National Institutes of Health
NSF	National Science Foundation
NSF-RANN	National Science Foundation-Research Applied to National Needs
ONR	Office of Naval Research
PSEF	Pennsylvania Science and Engineering Foundation
RC	Research Corporation
UEC	United Engineering Council
U of P	University of Pennsylvania
USA	United States Army
WRC	Welding Research Council

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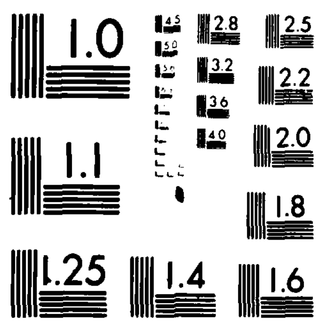

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